SORBED AND SOLUTION PHOSPHORUS AND THEIR RELATIONSHIPS TO CROP RESPONSE

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By

S.S. Soundararajan

Dissertation Committee:

Robert L. Fox, Chairman
Bruce J. Cooil
Samir A. El-Swaify
James A. Silva
Goro Uehara

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ABSTRACT

Adsorption of phosphorus from aqueous solutions by several Hawaiian and Indian soils was studied in relation to P concentration, equilibration time, ionic environment and temperature. The effect of a prior P application on the sorption of P subsequently applied was studied using samples of a calcareous Superstition sand, previously used in a pot experiment in which P was a variable. The phosphate sorption curves were used for estimating the P requirement of soils for maximum crop growth of pearl millet (Pennisetum typhoides) and Desmodium (Desmodium intortum).

To approximate equilibrium it was necessary to allow six and eight days reaction time for acid soils and calcareous montmorillonitic soils respectively. Substitution of K for Ca in the equilibrating solution always resulted in increased P adsorption. Also an increase in the salt concentrations (KCl and $CaCl_2$) increased P retention by soils.

Phosphate sorption isotherms suggested that for non-calcareous soils at low solution P concentrations, P sorption was limited mostly to monolayer adsorption by P reactive sites. At higher concentrations an abrupt increase in P retention occurred. The shape of the isotherms suggested either presence of groups of P reactive sites which are energetically different and/or multilayer adsorption.

In calcareous soils at low solution P concentrations the mechanism of P retention seems to be adsorption, with precipitate formation, probably $CaHPO_4$, becoming important as P concentration in solution increased. Provided the equilibration time is long, phosphate added to a calcareous soil, even in low amounts, may form nuclei for additional P precipitation.

Almost all of the P adsorption and desorption isotherms followed the Langmuir equation. This enabled the calculation of P adsorption maxima, which were found to be a good means of expressing the P buffering capacity of soils. Thermodynamic studies showed the differential heats of P adsorption to vary after 0.8 fractional saturation of P reactive sites.

Phosphate sorption curves were used as a basis for fertilizing soils on which millet was grown. The equilibrium solution P concentrations at which 95 % maximum yields occurred varied with soils. Still it might be possible to use a general solution concentration value (0.6 ppm) for most of the agricultural soils as their P adsorption maxima are usually < 2600 ppm. The percentage saturation of the P adsorption maximum for 95 % yields of millet was inversely related to the adsorption maximum. Yields of Desmodium in comparison with millet showed an interaction existing between crops and adjusted solution P concentrations required for maximum yields in different soils.

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INTRODUCTION

The tendency of Hawaiian soils to sorb large amounts of phosphorus makes that nutrient an important factor controlling crop production. Although numerous reports, seeking to elucidate the processes involved have appeared in the literature beginning before 1902 (Crawley, 1902), the complexity of the problem warrants further study. Recent phosphorus research in Hawaii has been geared towards applying specialized P fertilization practices for maximum economic returns. Thus massive P fertilizer application was tried with some success by Young and Plucknett (1965, 1966). The principle involved in their experiment was to "quench" the P fixation complexes by a heavy initial P treatment, with phosphorus left over to maximize yield.

At this point it is appropriate to consider the factors that govern the supply of P to plants. They are intensity, kinetic, capacity and diffusion factors. It is generally agreed that crops derive P from the soil solution. The concentration of P in solution at any particular time is the intensity factor. As roots continue to absorb P, the solution is replenished with P desorbed from the solid phase. The rate of P release is a kinetic factor. The capacity of the soil to renew the solution with P, as P is taken up by the plant is a capacity factor, It is related to the amount of sorbed P in the soil. Since the effective volume of soil that supplies P is small, as the zone is depleted, replenishment involves a net transfer of P by diffusion. Processes associated with this kind of ionic movement are collectively termed the diffusion parameter.

An ideal study on P supply patterns and P requirement of soils should assess all of the above factors. The investigation should seek to understand the mechanisms involved, so that generalization can be made about prudent P fertilization practices.

The intensity parameter can be estimated by determining P concentration in solution or by evaluating the phosphate potential. The kinetic factor can be studied using anion exchange resins which serve as a sink for P, thus simulating plant removal of that nutrient. Assessment of buffering capacity involves the measurement of P sorption by soil at various P concentrations in solution. The diffusion factor is estimated as with other anions. However, the diffusion equation needs to be corrected for adsorption and precipitation of P.

All the four parameters determine P flux to plants; but, P concentration in solution has a direct bearing on crop uptake. The initial concentration of P depends on the relative saturation of the P adsorption capacity of the soils. The kinetic factor is not considered to be limiting as the rate of P release is purported to be 250 times greater than the plant absorption rate (Fried, et al., 1957). Many investigators have shown that P diffusion is proportional to the intensity and capacity factors. So, an estimate of P concentration in solution along with the magnitude of P sorption by soils should indirectly account for diffusion also. It can be inferred from the above observations that an estimate of two parameters, intensity and capacity factors, may adequately describe the P status and P requirement of soils.

Early attempts to describe the phosphorus status of soils were concerned with finding chemical reagents to proportionately extract P,

which was available to plants. To estimate exchangeable P, a measure of plant available P, anion exchange resins were used. Later, tracer techniques were also employed. All of these methods are limited in their usefulness as they make only an indirect assessment of the P requirement of soils for optimum crop growth. Also the validity of the approach over a wide range of soil conditions is questionable. An additional disadvantage in using chemical extractants is their tendency to redistribute the P compounds after they have been dissolved.

Recent approaches, however, are attempts to directly assess the P requirement of soils for near maximum crop yield. In this regard Beckwith (1965) proposed determining sorbed P at a standard supernatant solution concentration (0.2 ppm). Woodruff and Kamprath (1965) suggested the possibility of grouping soils based on the P adsorption maximum as calculated using the linear form of the Langmuir equation and the equilibrium solution concentrations of P. The use of adsorption isotherms have an advantage over conventional methods, since the isotherms take into consideration both intensity and capacity factors. Although the above approaches appear promising there have not been enough experiments conducted, using wide range of soils, either to confirm or discount their usefulness.

The present study was undertaken to investigate the applicability of Beckwith's hypothesis and to develop a better understanding of the relationship between relative P saturation and soil P availability to plants. The study also embodies an inquiry on surface reactions occurring between soil surface and solution interface at different P concentrations.

REVIEW OF LITERATURE

The bulk of the inorganic P in soil is present as sparingly soluble P compounds and adsorbed P. Phosphorus adsorption occurs, on the surface of clay minerals, aluminum hydroxide and hydrated iron oxides in acid soils and largely on $CaCO_3$ in calcareous soils, because of the residual attractive forces present at the surface of these solids. Adsorption differs from precipitation in that in adsorption the coordinating elements which form the surface still remain as the constituent of the corresponding hydroxides oxides or carbonates (Hsu, 1964).

A preponderance of evidence suggests that the initial rapid P removal by soils from solution is mainly an adsorption reaction rather than precipitation (Davis, 1935; Dean and Rubins, 1947; Burd, 1948; Low and Black, 1950; Fried and Dean, 1955; Blanchet, 1959; Rennie and Mckercher, 1962 and Muljadi, et al., 1966). Hsu (1964) believed that P reaction with hydroxides and oxides of aluminum and iron is a surface reaction involving adsorption. The following arguments were put forward in support of his contention. (i) The amorphous aluminum hydroxides and iron oxides are highly adsorptive resulting in very rapid P depletion from solution. (ii) At pH values of 5 and above aluminum and iron activity in solution is very low and yet fixation occurs. (iii) If phosphate removal from solution is a precipitate reaction, the dissolution of one part of the precipitate should not affect the solubility of the rest of the crystals, which is not the case in surface reaction occurring in soils, where the relative saturation is important in deciding the P concentration in solution (Islam, 1956; Cole and

Olsen, 1959; Islam and Rahman, 1959; Rennie and McKercher, 1959).

Numerous other reports indicate that P concentration in solution is not in agreement with the solubility products of sparingly soluble P compounds, purported to be present in soils (Wild, 1954; Chakravorthy and Talibudeen, 1962; Hagin and Haden, 1962; Bache, 1963). Nevertheless, P is not held by adsorption alone. Considering the latent P supplying power of soils, especially in calcareous soils, sparingly soluble P must also play an important role (Bjerrum, 1936; Metzer, 1940; Cole and Jackson, 1950; Bradley and Sieling, 1953; Chang and Jackson, 1957; Hemwall, 1957; Lindsay and Moreno, 1960; Kajwada, 1964). However, regardless of the mechanisms, the behavior reflected in a "sorption isotherm" has found to be useful for practical conclusions on P availability, and so, if for no other reason, further studies on P adsorption can be justified on the practical usefulness of this approach. In the review presented here emphasis is on P adsorption in relation to its availability to plants, with a brief discussion on mechanisms of P adsorption by soils.

P Adsorption Studies

Methodology

One needs to exercise caution while interpreting and comparing P adsorption isotherms since insufficient effort has been made to standardize procedures. Different equilibration times and ionic environments have been used by various researchers. Table 1 gives results of equilibration studies in various salt mediums and for various periods of equilibration tried. The operational definition, especially

Table 1. Ionic environments and equilibration times used by various authors for constructing P sorption isotherms

Year	Author	Ionic environment	Equilibration time (hours)
1935	Davis, L.E. (6)	KH_2PO_4 and K_2HPO_4	528 (22 days)
1946	Kurtz, T., et al. (11)	NaH_2PO_4	24
1950	Low, P.F., and C.A. Black	KH_2PO_4	1.5
1957	Olsen, S.R., and F.S. Watanabe (17)	KH_2PO_4 at pH 7	24
1959	Rennie, D.A., and R.B. McKercher (20)	KH_2PO_4 at pH 7	6
1960	Thompson, E.J., et al. (21)	KH_2PO_4 at pH 7	24
1962	Hsu, P.H., and D.A. Rennie	0.4 N NaCl + NaOAc + NaH_2PO_4	0.5
1964	Hsu, P.H.	NaOH + NaH_2PO_4 at pH 7	~6
1964	Onikura, Y. (12)	0.1 N Acetic acid + NaOAc + NaH_2PO_4 at pH 7	20
1965	Beckwith, R.S. (3)	NaOAc + NaH_2PO_4 pH 5.1-5.2	16
1965	Kurtz, T., and J.P. Quirk (12)	KH_2PO_4 pH 6.2	18
1965	Woodruff, J.R., and E.J. Kamprath (22)	$Ca(H_2PO_4)_2$ pH 7	24
1967	Muljadi, D., et al.	KH_2PO_4 Different pH's.	24 and 48
1967	Ozanne, P.G., and T.C. Shaw (19)	0.01 M $CaCl_2$ + $Ca(H_2PO_4)_2$	17
1968	Fox, R.L., et al. (7)	NaOAc + NaH_2PO_4 pH 5.1-5.2	144 (6 days)
1968	Gunary, D., and C.D. Sutton (10 A)	KH_2PO_4	18
1968	Ozanne, P.G., and T.C. Shaw (19)	0.01 M $CaCl_2$ + $Ca(H_2PO_4)_2$	17
1969	Bar-Yosef, B.	0.01 N KCl + KH_2PO_4	96
1970	Barrow, N.J. (4)	0.01 M $CaCl_2$ + KH_2PO_4	24
1970	Fox, R.L., et al.	0.01 M $CaCl_2$ + $Ca(H_2PO_4)_2$	144
1970	_____ and E.J. Kamprath (7)	0.01 M $CaCl_2$ + $Ca(H_2PO_4)_2$	144
1970	Gunary, D. et al (8)	0.01 M $CaCl_2$ + KH_2PO_4	18
1971	Fox, R.L., and E.J. Kamprath	0.01 M $CaCl_2$ + $Ca(H_2PO_4)_2$	144

the ionic environment, deserves more attention since ionic strength and kind of cations appreciably influence P adsorption and P remaining in solution.

Numerous reports have appeared in the literature reporting the depressing effect of salts on P solubility (Clark and Peech, 1960; Larsen, 1965, 1966; Fox, 1970; Jenson, 1970; Peaslee and Phillips, 1970). Aslyng (1954) found that increasing electrolyte (KCl) concentration was associated with lower pH of soil suspensions and lower P concentration in solution. Schofield (1949) and Aslyng (1954) ascribed this effect to co-adsorption of phosphate along with exchangeable cations. Clark and Peech (1960) confirmed the earlier results and put forward the same explanation. Russell (1961) in his discussion on anion holding power of soils explained the influence of salt concentration on anion adsorption as follows.

> "The positive charges (on soil surfaces) need not necessarily be neutralized by simple anions if they are very close to negatively charged spots, for if the electrolyte concentrations is not too high, the double layers around the positive and negative spots will interpenetrate with a consequent decrease in the cation concentration in the interpenetrating layers. Hence such a system can only show its maximum ab(d)sorption for anions when the electrolyte concentration is sufficiently high to compress the double layers so much that there is no interpenetration."

Recently Hingston, et al. (1967) reported that maximum adsorption of anions at a particular pH is insensitive to changes in ionic strength. This conclusion was supported by the findings of Barrow (1970). Thus increased P adsorption in the presence of salts may be explained by pH and charge density changes along with co-adsorption phenomenon. Still it is ~~of~~ importance to point out ~~here~~ that ~~the~~ pH change ~~need~~ do not necessarily influence ~~the~~ P adsorption in ~~all~~ soils. For instance Fox

(1971) could not detect any appreciable change in P adsorption by change of pH in a Low Humic Latosol from Hawaii. The author found pH increase from 4 to 8 to have no influence on P sorption by a Humic Latosol; a slight decrease in P adsorption by a Humic Ferruginous Latosol; and a very appreciable decrease in Hydromorphic soil from Hawaii. Similar observations were made by Lai and Okazaki (1970).

Calcium has a greater depressing effect on P solubility than K or Na (Ellis and Truog, 1955; Fried and Dean, 1955; Olsen, et al., 1960; Gunary, 1964; Tobia and Milad, 1964; Fox and Kemprath, 1970). Lehr and Vansemael (1952) using Dutch soils reported that when the same anion was used P solubility was increased in the order Ca < Mg < K < Na. Aslyng (1954) also found the concentration of P in solution to be higher when the soil was extracted with KCl than $CaCl_2$. One explanation offered for lower solubility of P in presence of Ca is the formation of calcium phosphate compounds on the surface of the clay particles by the exchangeable calcium (Ellis and Truog, 1955; Russell, 1961).

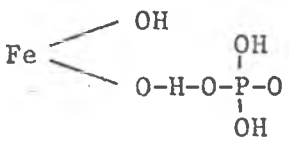
P Adsorption in Acid Soils

The complexity of the mechanisms of P adsorption in soils can be surmised from the fact that most of the investigators have used commercial clays or pure oxides and hydroxides of Fe and Al, rather than soil itself. In the light of the recent findings of Jones, et al. (1969), concepts regarding the role played by clay minerals, as represented by pure clays needs reevaluation. Jones showed that clay particles of Hawaiian soils are coated with thin layers of gels, thought to be composed largely of non-crystalline hydrated alumino silicates with some iron. Fox, et al. (1970) also added evidence to this observation. In

some soils these coatings may be more responsible for surface reactions than the crystalline materials (Saunders, 1965).

It has long been recognized that the hydroxides and oxides of iron and aluminum, and edge aluminum present in clay minerals are responsible for P fixation. The suggested mechanism is exchange of phosphate for hydroxyl ions (Mattson, 1931; Heck, 1934; Ravicovitch, 1934; Scarseth, 1935; Pugh and Dutoit, 1936; Murphy, 1939; Stout, 1940; Kelley and Midgley, 1943; Dean and Rubins, 1947; MacAuliffe, et al., 1948; Haseman, et al., 1950; Low and Black, 1950; Muljadi, et al., 1966; Kafkafi, 1968).

Hsu and Rennie (1962) reported that P will be adsorbed by aluminum hydroxide, when the attraction between aluminum hydroxide and phosphate is strong enough to remove the surface hydrosyls already present. They also pointed out that the number of surface hydrosyls present may not be constant. Jacobs (1964) studied the interaction between positively charged hematite and phosphate anions. He suggested that P adsorption occurs as a result of neutralization of hydrogen ions responsible for the surface charge, by $H_2PO_4^-$ ions with the formation of H_3PO_4 molecules. The reaction was represented as below.



Kelley and Midgley (1943) observed that high temperature treatments greatly reduced P fixation by hydrated iron oxide (FeO^+). This can be explained now based on Rollinson's report (1956), that heating may have converted many of the "ol" groups (-M<OH>M-) to "oxo" groups (-M<O>M-) the latter being much less reactive. Mekaru (1969)

indicated that P adsorption capacity of soils does not depend alone on the amount of free iron oxide but also on the reactive nature of the oxide surface. He attributed the very high P fixing capacity of Hydrandepts (Hydrol Humic Latosol) of Hawaii to their more active hydroxo, aquo and ol co-ordination along with higher amount of iron oxide, compared to less reactice "oxo" groups of other less hydric Hawaiian Latosols.

Harward and Reisanauer (1966) stated that adsorption of an anion on a metal complex depends on its ability to coordinate with the metal cation; thus suggesting ligand exchange. Hingston, et al. (1967, 1968) advanced the concept that phosphate is adsorbed specifically (on goethite) irrespective of net positive or negative charges as determined by Δ pH (Δ pH = pH in 1N KCl - pH in H_2O paste). Mekaru (1969) working with Hawaiian soils found that the above concept agreed with observed pH changes and CEC changes associated with anion adsorption. He presented a model for P adsorption on iron oxide based on the mechanism proposed by Hingston, et al. (1967, 1968) (Fig. 1).

While adsorption is considered to be the main mechanism for P fixation of soils at solution concentrations of less than 10 ppm (Hsu and Rennie, 1962; Johansen and Buchanan, 1957) P removal from solutions of higher than this concentration is still a matter of controversy and the phenomenon is less clearly understood. Apart from the classical theory of precipitate formation the following postulations have been advanced recently to explain the process. According to Hsu and Rennie (1962), at very high concentrations adsorption occurs at the new surfaces exposed by phosphate adsorbed already. Kafkafi, et al. (1967)

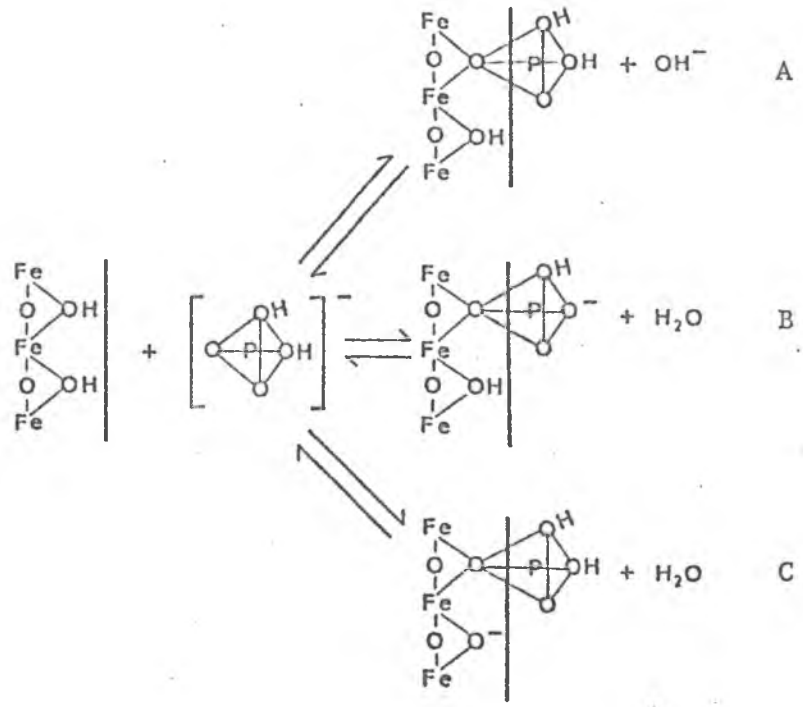


Fig. 1-Probable mechanism of phosphate adsorption at low solution P concentrations. pH increase is predicted by (A) but not by (B) or (C). In (B) the surface acquires a negative charge by proton transfer by the sorbed phosphate, whereas in (C) the negative charge arises from proton transfer directly from surface hydroxyl.

(Proposed mechanism of Hingston, et al., 1967, 1968. Source - Mekaru, 1969).

stated that fixed phosphate may increase the affinity of the kaolinite surface for additional P though no explanation was given about the mechanism.

It has been shown that P adsorption increases negative charge of soil surfaces and so increases cation exchange capacity (Toth, 1937; Coleman and Mehlich, 1948; Yoshida, 1960; Hingston, et al., 1967; Mekaru, 1969). This may lead to more cation adsorption if cations are present in solution, often in excess of what is needed to neutralize the negative charges which may then ultimately result in additional P adsorption.

P Reactions in Calcareous Soils

In calcareous soils calcium carbonate plays a dominant role in P solubility through its effect on soil pH, by providing a reactive surface, and by providing Ca, a common ion (Cole, et al., 1953; Arambarri, 1967). It is generally agreed that $CaCO_3$ depresses P solubility, and the suggested mechanism is adsorption at low concentration followed by precipitation (Boischot, et al., 1949, 1950; Cole, et al., 1953). Cole, et al. (1953) reported that at concentrations up to 9 ppm the reaction of P with $CaCO_3$ is adsorption to form a monolayer. This is followed by precipitation of dicalcium phosphate or other compounds with similar properties. Evidences for precipitate formation have come from experiments conducted at very high P concentrations. For example Kittrick and Jackson (1956) used 1 M solutions of Na or K phosphates and Hanway and Scott (1959) employed 4.5 M phosphate solution. This concentration in soil solutions has never been reported except maybe in the vicinity of fertilizer granule. However, there is evidence to show P concentration to be up to 0.19 M at a distance of 30 mm from the zone

of fertilizer placement (Lindsay and Stephenson, 1959). Many authors have claimed that one of the more important initial precipitation products is dicalcium phosphate dihydrate (Brown and Lehr, 1958, 1959; Bouldin, et al., 1960; Hinmann, et al., 1962; Das and Datta, 1966, 1967; Bill and Black, 1970). Murrmann and Peech (1968) reported fluorapatite to be the ultimate reaction product of the applied super phosphate in limed soils.

Though petrographic studies have shown the presence of dicalcium phosphate dihydrate in soils near fertilized zones (Lehr, et al., 1959), the solution concentration of P is not found to be in agreement with the solubility product of the compounds (Wild, 1954; Black, 1969). The discussion of Boischot, et al. (1950) gives a basis for explaining the above observations. As the precipitate formed redissolves, phosphate is redistributed over the surface of $CaCO_3$ particles and adsorption may take place. This adsorbed P may be exchangeable and it is the amount of labile P and relative saturation of the adsorptive surfaces which decide P concentration in solution. In view of this argument the following observations are of interest. In calcareous soils Arambari (1967) showed that the amount of exchangeable P increased with increasing area of adsorbing surface. Cole and Olsen (1959) reported that P solubility in calcareous soil is directly related to the amount of surface area and per cent saturation of these surfaces.

Effect of P Adsorption on the Release of Silicate and Sulfate

Phosphates, silicates and sulfates are held by soil surfaces by specific adsorption (Hingston, 1967). The displacing strength of an anion depends on its ability to coordinate with metal cation (Harward

and Reisenauer, 1966). The results of Hingston, et al. (1967, 1968) indicate that phosphate is held more strongly than the other two anions, probably because of its ability to render the surface charge of solids more negative. It is reasonable to suppose then, that P adsorption will release silicate and sulphate anions in solution, along with the displacement of hydroxyls.

As early as 1931, Mattson reported that phosphate ions strongly displace silicates. Similar observations were made by Davis (1935) and later on by other workers (Toth, 1937; Low and Black, 1948, 1950; Reifenberg and Buckwold, 1954). Kafkafi (1968) indicated that applied silicates increased pH and also released P from kaolinite. Roy (1969) reported increased native silica solubility as P was adsorbed by Hawaiian Latosols. Silicon release as P was sorbed was in the following order: Wahiawa > Kapaa > Akaka.

Harward and Reisenauer (1966) stated that sulfate is more weakly held than phosphate. Many authors have reported that phosphate displaced sulfate or reduced sulfate adsorption (Ensminger, 1954; Kamprath, et al., 1956; Bornemisza and Llanos, 1960; Chao, et al., 1962). Some procedures for evaluating sulfur status of soils make use of this relationship, and use of phosphate solutions in lieu of water have been recommended for extracting sulfur (Chesnin and Yien, 1950; Spencer and Freney, 1960; Fox, et al., 1964). Also the observation that phosphate tended to enhance sulfur movement in soils can be explained by anion exchange. However, it is important to note that exchange between phosphate and other anions is not a stoichiometric reaction (Nagarajah, et al., 1968).

Fitting P Adsorption Data to Theoretical Models

As early as 1935, Davis described the adsorption of P by non-calcareous Hawaiian soils by the function $\Delta P = kP_E^{1/3}$, where ΔP equals the change in concentration and P_E the equilibrium concentration of P. Later on many other researchers also found that the P adsorption data could successfully be expressed using Freundlich equation which has the form

$$X/m = KC^{1/n}$$

which may be expressed as a linear equation by use of the logarithmic scale.

$$\text{Log } X/m = \text{Log } K + \frac{1}{n}\text{Log } C$$

where

X/m = Amount of P adsorbed/unit weight of soil

C = Equilibrium solution concentration

K and n are constants

Olsen and Watanabe (1957) were among the first to use the Langmuir equation for phosphate sorption studies. This equation was developed using kinetic consideration to describe mono-molecular adsorption of gases on solid surfaces. The Langmuir equation has the advantage of permitting the calculation of adsorption maxi~~mum~~ a. The equation as applied for solid : solution system can be given as

$$X/m = \frac{AbC}{1+AC} \qquad (1)$$

Where X/m = Amount of P adsorbed/unit weight of soil

A = Constant related to bonding strength

b = Adsorption maximum

C = Equilibrium concentration

in linear form

$$\frac{C}{X/m} = \frac{1}{Ab} + \frac{C}{b} \qquad (2)$$

As can be visualized from equation (1) at very high values of C, X/m approaches b, monolayer coverage of the adsorbent. Despite the many assumptions involved (Adamson, 1960) this equation maintains its popularity because of the ease with which adsorption maximum can be calculated (Cole, et al., 1953; Rennie and McKercher, 1959; Weir and Soper, 1962; Sutton and Larsen, 1964; Harter, 1968). However, one limitation of applying the Langmuir equation is its failure to follow a straight line at higher solution concentrations. To rectify this, Gunary (1970) introduced a square root term as follows.

$$\frac{1}{X/m} = B + \frac{A}{C} + \frac{D}{\sqrt{C}}$$

B, A, and D are constants.

This equation was not based on theoretical considerations and no practical advantage over the usual form of the Langmuir has been reported.

Thermodynamics of Adsorbed and Solution Phosphorus

Phosphate potential. Schoefield (1955) postulated that the chemical potential of soil phosphate (referring to the ease with which phosphate could be removed) would provide a good measure of P availability. Then the energy needed to withdraw P becomes more important than the

concentration of P in solution. The suggested equation for calculating the phosphate potential is

$$\text{Phosphate Potential} = 1/2\ pCa + pH_2PO_4$$

The emphasis is on the activity of phosphate rather than the concentration in solution. For extraction, 0.01 M $CaCl_2$ was suggested since cation exchange is minimized by using Ca, and chloride at this concentration has almost no specific anion replacing power. Schoefield's suggestion on possible uses of the phosphate potential in soil research unleashed numerous publications both supporting (Aslyng, 1954; Clark and Peech, 1960; Lemare, 1960) and discounting it (Moser, et al., 1959; Thompson, et al., 1960; Withee and Ellis, 1965; Wilson, 1968; Redmond, 1969). Ramamoorthy and Subramanian (1960) introduced the term "equilibrium phosphate potential." Instead of 0.01 M $CaCl_2$ extraction the same solution containing graded amounts of P was used for estimating phosphate potential.

The thermodynamic approach for studying P availability to plants, based on free energy considerations assumes P to be bonded to soil surfaces instead of freely diffusible (Bache, 1965). Reaction kinetics of P adsorption and desorption have suggested that different portions of phosphate are held on surfaces with widely different free energies (ΔG) MacAuliffe, et al., 1948; Haseman, et al., 1950; Low and Black, 1950; Talibudeen, 1960). Shapiro and Fried (1959) illustrated the presence of two forms of soil P, one tightly held and one held with relatively less energy. Onikura (1964) also reported similar results. Muljadi, et al. (1966), studying with well defined (soil) mineral systems suggested

three regions in the P adsorption curve related to the affinity of phosphate for energetically different types of reactive sites.

Heat of P adsorption ($\overline{\Delta H}_{X/m}$): Adsorption of P has been shown to be an endothermic reaction (Low and Black, 1950; Beaton, et al., 1960; Muljadi, et al., 1966) and unlike adsorption of gases on solids an increase in temperature results in increased P adsorption. There are two ways of calculating the energies of adsorption; colorimetrically and by employing the Clausius-Clayeperon equation.

The differential heat of adsorption can be described as follows (Everett, 1950). If Q is the amount of heat absorbed on adsorption of m moles of P then the differential heat of adsorption (D.H.A.) is equal to $\partial Q/\partial m$. The heat of adsorption calculated using the isotherms at different temperatures is termed "isosteric heat of adsorption" ($\overline{\Delta H}_{X/m}$) and is similar to D.H.A. The subscript X/m denotes the heat of adsorption at that particular surface coverage. The Clausius equation used for calculating $\overline{\Delta H}_{X/m}$ can be presented in the form

$$\frac{\ln C}{dT} = \frac{\overline{\Delta H}_{X/m}}{RT^2}$$

where

C = Equilibrium solution concentration of P

T = Absolute temperature

R = Gas constant

Integrating on the assumption that the heat of adsorption is independent of T

$$\int d \ln C = \frac{\overline{\Delta H}_{X/m}}{R} \int T^{-2} dT$$

$$\ln C = \frac{\overline{\Delta H}_{x/m}}{RT} + C'$$

Where C' is the Integration constant

Shapiro and Fried calculated heats of adsorption to be 12 and 14 K calories for two acid soils and 7 K calories for a calcareous soil. Muljadi, et al. (1966) however, reported very small values of isosteric heat of adsorption at their "region II" for kaolinite, gibbsite and pseudoboehmite.

The following discussion is based on chemisorption studies conducted with gases (Joyner and Emmett, 1948; Everett, 1950; Gles, et al., 1960; Kington and Smith, 1964; Smith and Ford, 1965; Davis and Pierce, 1966), where the adsorption process is exothermic. When a parallel is drawn between an exothermic and an endothermic reaction, like P adsorption on soil surfaces, the trend in heat of adsorption will be in the reverse direction.

Since soil surfaces are heterogeneous, changes in heat of adsorption with surface coverage are likely to occur. When phosphate ions come into contact with the adsorbent, the chances are for the most energetic sites to be occupied first (Tompkins, 1950), which require the lowest heat of adsorption. The system will be in a more favored state thermodynamically when $\overline{\Delta H}$ is relatively small. As the P concentration in solution increases, fewer active sites on the adsorbate are occupied and the heat of adsorption also increases. Based on the above arguments P adsorbed at higher concentrations and requiring higher heats of adsorption should be loosely held compared to that portion of adsorbate initially adsorbed.

Desorption of Phosphorus

The literature on P desorption is meagre although P release from soil is very important for plant uptake. In the light of recent findings of Hingston, et al. (1967, 1968) the procedure of using water or solution of indifferent anions like chloride for desorbing P is not incontestable, as plants may be getting their P by secreting anions like citrates, tartarate, and oxalate (Jenny and Grossenbacher, 1963; Rovira, 1965; Brams, 1969). Nevertheless, these studies are useful for reflecting in a relative way the P supply behavior of soils.

It has been reported that P sorption isotherms show hysteresis on desorption, and depending on the region of the isotherm the adsorbed P may or may not be reversible with reference to concentration in solution (Muljadi, et al., 1966). Fox and Kamprath (1970) found a very large hysteresis effect when the P sorption capacity of the soil was very high. Kafkafi (1967) reported that on washing with 0.01 M KCl, some of the P adsorbed ceased to be exchangeable. However, on contact with a more concentrated P solution the previously fixed P became completely isotopically exchangeable. This is possibly due to the ability of concentrated P solution to make the soil surface more negative, and so self exchange of P took place. Phosphate desorption can also be described by the Langmuir equation similar to adsorption isotherms. Fried and Shapiro (1956) used water as the extractant, and found that P dissolution was like desorption for four soils while on successive extraction of three soils, the concentration of P was maintained at a reasonably constant value which suggested the dissolution of some specific compound.

Studies on P Availability to Plants

The phosphorus supply to plants is governed by intensity, capacity, kinetic and diffusion factors. These factors have been correlated with P uptake either individually or in combination (Aslyng, 1954; Baker, 1964; Mattingly, 1965; Williams, 1965; McConaghy, et al., 1966; Gunary and Sutton, 1967; Ozanne and Shaw, 1967, 1968). All the four factors are inextricably linked although sometimes, because of special interests of the investigator the importance of only one factor has been stressed rather than considering the parameters in perspective.

The immediate source of P for the plant is the solution, and thus the intensity factor (solution concentration of P) has direct bearing on P supply to plants. The initial P concentration is determined by the relative saturation of surfaces which adsorb phosphate (Islam, 1955, 1956; Cole and Olsen, 1959; Rennie and McKercher, 1959). Maintenance of that concentration, especially during extraction by plant roots depends on the kinetic factor, buffering capacity and the diffusion factor.

P desorption studies have been used to investigate the P supplying power of soils including the rate of P release (kinetic factor). Fried, et al. (1957) found that the rate of adsorbed P release in soils is 250 times greater than the plant absorption rate and so the kinetic factor was not considered to be limiting. Olsen and Watanabe (1963) realizing the importance of effective soil volume, the volume of soil actually explored by plant roots, used tracer P and excised corn roots to study this aspect of phosphate supply. They also made observations similar to those of Fried, et al. (1957). Following the procedure of Amer, et al. (1955), Cooke and Larsen (1966) studied the rate constants using a

number of different soils. The rate of P release was described according to the equation

$$P = R\sqrt{t} + b$$

Where P = Total P released

t = Time

R and b are constants

They obtained a good correlation between the rate of P release (R) and P uptake by rye grass and concluded that the rate of replenishment of P is important and must form a part of any comprehensive study of the phosphate status of soils.

The diffusion of P occurs, essentially in the liquid phase and to a very small extent perhaps, along the solid phase (Nye, 1966). A diffusion coefficient is usually used to describe the diffusion process. Lewis and Quirk (1967) reported that the apparent diffusion coefficient (D_e) in soil solution strongly depends on the amount of P adsorbed and P concentration in solution. The suggested equation was,

$$D_e = D_p + \frac{\text{P in solution}}{\text{P Total}}$$

where

D_e = Diffusion coefficient as observed when P diffusion occurs in soil solution

D_p = Diffusion coefficient in porous system without P adsorption on surface

Keeping other factors like moisture content, tortuosity and rate of uptake by plants constant, the above equation can be reduced to a simple

relationship as diffusion occurring is proportional to the intensity and capacity factors (Labile P). There is evidence in the literature suggesting that the kinetic factor is also related to exchangeable P present although the importance of the rate factor itself has not been established beyond doubt.

Gunary and Sutton (1967), Barrow (1967) and Ozanne and Shaw (1967) were able to account for about 80 per cent of the variation in P supply pattern of soils by evaluating capacity and intensity parameters alone.

The above arguments lead to the conclusion that the over-riding factors in P supply are the intensity and capacity parameters, and that kinetic and diffusion factors are indirectly accounted for when these are estimated.

Intensity Factor

A wealth of literature supports the theory that crops grown on soil derive P from the solution phase (Larsen, 1967; Black, 1969; Omanwar and Robertson, 1970). Wild (1964) claimed that "with solutions about the same composition as those in soil, it is the phosphate concentration and not the potential which determines P uptake by plants." Olsen, et al. (1969) using alkaline and calcareous soils found that P uptake by corn was a function of log[P] in solution. Gunary and Sutton (1967) obtained a good correlation between log P concentration and P uptake by rye.

Since solution P has a direct bearing on crop uptake, efforts have been made to develop procedures for estimating P requirements of soils for near maximum crop growth, based on P adsorption at particular solution concentrations. Following the lead of Andrew, et al. (1965), who observed the approximate critical concentration of P in solution for

optimum growth of legumes is about 0.2 ppm, Beckwith (1965) proposed that estimates of P needs of soils be based on measurement of P adsorbed at a standard supernatant concentration of about 0.2 ppm. Beckwith used sodium acetate and sodium phosphate as the medium for equilibrating soils. The equilibration time was 16 hours.

Ozanne and Shaw (1967) ran P adsorption isotherms in 0.01 M $CaCl_2$ and found that P sorbed at 0.3 ppm P in solution correlated closely ($r = 0.97$) with the P requirement for maximum obtainable yield of clover. They also claimed that the standard value (0.3 ppm) was applicable over a wide range of cultural practices. Fox, et al. (1968) followed the procedure of Beckwith for constructing P sorption isotherms of Hawaiian soils except that the samples were equilibrated for 6 days. They reported that P sorbed at 0.2 ppm P in solution was consistent with observed P needs, for some Hawaiian soils. Another report (Fox and Kamprath, 1970) indicates that the same value was applicable for green house grown pearl millet, in spite of a different ionic environment (0.01 M $CaCl_2$) that was used for running P sorption isotherms. Not all reports favor the above approach. Olsen and Watanabe (1963) stated that P diffusion becomes limiting more rapidly in sandy soils than in clays and so lighter soils may require higher P concentration in solution than heavy clays. The findings of Woodruff and Kamprath (1965) support the above hypothesis. They observed the required P concentration for millet is between 0.3 to 1.2 ppm depending on the adsorption capacities of the soils. They based P requirement on the percentage of P saturation in relation to the adsorption maximum as discussed in the following section.

A close scrutiny of the above reports suggests that Beckwith's idea of estimating P requirement at a particular solution concentration will be a good tool, so long as the aim is to group similar soils together (as stressed by Beckwith himself) rather than attempting to establish an unique value for all soils.

Capacity Parameter

The capacity of soils to maintain P concentration in solution is of ~~equal~~ equally as importance ~~like~~ as the solution concentration itself. Localized depletion and exhaustion of P occurs readily when the P buffering capacity is low. Many researchers have tried using E values, the exchangeable phosphate adsorbed on the soil particle surface (McAuliffe, et al., 1948; Barbier, et al., 1954; Talibudeen, 1957, 1958; Olsen, et al., 1962) and L values as a measure of capacity factor (Larsen, 1952; Russell, et al., 1957, 1958; Nye and Foster, 1958; Larsen and Cooke, 1961; Baker, 1964; White, 1968).

Gunary and Sutton (1967) found the L value to be the best indicator of capacity factor and E value estimated in the laboratory to be a poor measure. Also, White (1968) reported that an increase in L value was consistent with increased P buffering capacity of soils. However, Russell, et al. (1957) discarded E and L values as poor measures of the capacity factor especially when contrasting soils were used.

Another means of measuring phosphate buffering capacity is by using P sorption isotherms. Beckett and White (1964) introduced the term phosphate potential buffering capacity (P.B.C.) and defined the term as the slope of the quantity-intensity relationship ($\Delta Q/\Delta I$). It is the relationship between change in sorbed P and the activity of phosphate.

Barrow (1967) measured buffering capacity of soils by calculating the tangent of the P adsorption line at 0.2 ppm equilibrium P concentration. Ozanne and Shaw (1968) defined phosphate buffering capacity of soils as the amount of the P sorbed between equilibrium solution concentrations of 0.25 to 0.35 ppm. By including buffering capacity in the correlation, in addition to bicarbonate soluble P, they were able to account for 83 per cent of the variation in P requirement compared to 39 per cent when the intensity factor alone was used.

An even more refined way of treating the subject is by applying the Langmuir equation. Many reports have shown that the Langmuir equation gives a good fit for P sorption data at low levels of equilibrium solution concentration (Olsen and Watanabe, 1957; Rennie and McKercher, 1959; Fox, et al., 1968), and the adsorption maximum calculated using this equation could be a good measure of the capacity factor.

Woodruff and Kamprath (1965), using soils with a wide range of chemical properties, found that soils with high P adsorption maxima required lower percentage P saturation for maximum growth of millet than soils with low phosphate adsorption maximum. Based on these inferences they postulated the possibility of grouping soils according to the percentage saturation of the adsorption maximum required for maximum growth. Fox, et al. (1968) reported that the P requirement of a high P fixing Hawaiian soil approximated one quarter saturation of the P adsorption maximum.

MATERIALS AND METHODS

Description of Soils Used

Seventeen soils representing a wide range of degree of weathering, thus very different in physical and chemical properties, were used in one or more of the experiments described. Eight soils belonging to six great soil groups were collected from the Hawaiian Islands. These are listed in Table 2 according to the old and new classification systems. Eight other soils representing four soil types, namely Black Soil, Red Soil, Low Level Laterite (Buchanan's Laterite) and High Level Laterite were brought from Tamil Nadu, South India. Also a set of eight samples of a calcareous Superstition Sand was obtained from California. The Superstition Sand samples had been treated with various amounts of superphosphate and had been left to equilibrate in the greenhouse, moistened but without plants, for six weeks.

Some general features associated with the experimental soils are presented in Table 3. A short summary of the characteristics of the soils used are given below. However, for a detailed description of the Hawaiian soils the reader is referred to "Soil Survey of the Territory of Hawaii" (Cline, 1955) published by the U.S.D.A., and for Indian soils the following references (Mariakulandai, A., and Venkataehalam, S., 1954; Pandey, 1969).

The Lualualei soil is a Dark Magnesium Clay (Typic Chromustert). It is of alluvial origin and has developed under semi arid conditions. Texturally it is a heavy clay and contains high amount of calcium sulfate and calcium carbonate.

Table 2. List of Hawaiian soils used according to the old and new classification systems

Soil Series	Old Classification (Great Soil Group)	New Classification (Sub Group)
Lualualei	Dark Magnesium Clays	Typic Chromustert
Molokai	Low Humic Latosol	Tropeptic Torrox
Wahiawa	Low Humic Latosol	Tropeptic Eutrusthox
Kapaa	Latosol Humic Ferruginous	Typic Gibbsihumox
Akaka	Hydrol Humic Latosol	Typic Hydrandept
Naalehu	Reddish Prairie	Typic Eutrandept
Maile	Latosolic Brown Forest	Typic Dystrandept
Hanipoe	Latosolic Brown Forest	Typic Dystrandept

Table 3. Some general characteristics of the soils used

Soils	pH					Surface P (ppm)	Chemical Extractable P (ppm)	Organic Carbon (%)	Exchangeable Al (ppm)	Important Secondary Minerals
	0.01 M $CaCl_2$	H_2O 1:2.0	1 N KCl Paste	H_2O Paste	ΔpH					
Hawaii Soils										
Lualualei	7.50	8.78	6.50	7.80	-1.30	29	84*	0.96	0.03	Montmorillonitic
Molokai	6.01	7.00	5.51	6.12	-0.61	196	126	1.90	0.01	Kaolinite
Wahiawa	5.77	6.62	5.60	5.92	-0.32	1	2	1.63	-	Kaolinite
Kapaa	4.03	4.83	3.98	4.19	-0.21	102	5	6.18	21.80	Gibbsite+Goethite
Akaka	4.05	4.00	4.23	3.99	+0.24	350	16	9.21	5.07	X-ray amorphous
Naalehu	5.70	6.60	5.48	6.38	-0.90	380	105	4.98	0.07	X-ray amorphous
Maile	5.39	6.60	5.68	6.02	-0.34	201	5	10.24	0.11	X-ray amorphous
Hanipoe	5.39	5.75	5.10	5.30	-0.24	481	382	9.68	0.08	X-ray amorphous
Indian Soils										
Black Soil, Coimbatore	7.71	8.15	6.18	7.29	-1.11	20	61*	0.49	0.07	Montmorillonite
Black Soil, Kovilpatty	7.00	8.40	6.12	7.61	-1.49	-	15*	0.34	0.07	Montmorillonite
Red Soil, Coimbatore	7.38	7.75	6.60	7.30	-0.70	40	34	0.28	0.02	Kaolinite
Red Soil, SVRP	7.00	7.80	6.20	7.31	-1.11	-	154	0.14	0.02	Kaolinite
Low Level Laterite, Pallathur	4.92	5.92	4.20	4.98	-0.78	-	111	0.62	9.20	Kaolinite
Low Level Laterite, Vallam	4.41	5.30	3.80	4.60	-0.80	20	7	0.33	19.35	Kaolinite
High Level Laterite, Doddabedda	4.50	5.45	3.94	4.81	-0.87	151	15	4.41	95.20	Kaoline+Gibbsite
High Level Laterite, Nanjanad	4.42	4.90	3.90	4.30	-0.40	-	160	1.82	117.75	Kaoline+Gibbsite

*Extraction of P by Olsen's Bicarbonate Method. Others by Modified Truog's Method.

Wahiawa (Tropeptic Eutrustthox) and Molokai (Tropeptic Torrox) represent the Low Humic Latosols of Hawaii. They developed from basalt and are acid in reaction. Though they are clays, they are highly aggregated and so their apparent textures are silty clay loams. The soils contain large amounts of iron oxides. Kaolinitic clays dominate the mineralogy and the magnitude of P fixation is comparable to that of pure kaolinite clays (Stout, 1940).

The Kapaa soil belongs to the aluminous Humic Ferruginous Latosol group (Typic Gibbsihumox). It is highly weathered and approaches the end products of tropical soil formation (Sherman, 1958). This soil is rich in Iron and aluminum oxides and also contain definite concretions of TiO_2.

The Naalehu (Typic Eutrandept), Maile (Hydric Dystrandept) and Hanipoe (Typic dystrandept) soils, representing Reddish Prairie and Latosolic Brown Forest great groups, developed from volcanic ash. The Latosolic Brown Forest soils however, have developed under heavier rainfall and are more acidic than the Reddish Prairie soil. The Si/R_2O_3 ratio of the Brown Forest soil may be as low as 0.2.

Akaka soil is a Hydrol Humic Latosol (Typic Hydrandept) and occurs in areas of very high rainfall (380-750 cm). It is highly hydrated, sometimes holding 250 to 350 % water on dry weight basis. On drying it becomes irreversibly dehydrated. Because of heavy leaching and low permanent charges, the bases have been reduced to very low levels unless recently limed, and soil reaction is strongly acid.

The Black soils of Tamil Nadu, India developed from basic rocks, rich in sodium-calcium felspars, under arid or semi arid conditions

(annual precipitation 45 cm). The soils contain gypsum crystals and concretions of calcium carbonate. The colloidal system is dominated by montmorillonitic clays, and though the clay content may amount to less than 40 %, the soil behaves like heavy clay when wet. Soil pH is about 8.0 and organic matter content is low. The silica sesquioxide ratio is more than 4.0.

The Red soils of South India originated from acid rocks containing about 65 per cent silica. Gypsum crystals are absent but there are rare occurrences of $CaCO_3$ as incrustations or as nodules. These soils contain approximately 12 % free oxides of Fe and Al. Red soils are mostly sandy loams with a very friable structure. Kaolin clays dominate the mineralogy and the soil reaction is either neutral or acidic.

The Low Level Laterites are similar to the laterites described by Buchanan (1807). These are very acid, infertile soils containing high amounts of iron and aluminum. The clay minerals are predominantly kaolins. The Si/R_2O_3 ratio is usually less than 1.0. Organic matter content is very low.

High Level Laterites have developed from gneissic rocks termed charnockite, with a few later dykes of olivine and norites. These are found at high altitudes (2,000 meters). Because of high precipitation (200 cm) the bases have been leached and soils are highly acidic (pH 5). These soils contain kaolins and appreciable amount of gibbsite.

B. Methods

1. P Characterization of Soils and pH Determinations

a. Surface P Estimation: For determining surface P, 5 g of soil

was equilibrated with 100 ml of P solutions, tagged with P^{32} for 6 days, with 30 minutes shaking in the mornings and evenings. Three drops of toluene was added to control microbial activity. After the equilibration time, total and radioactive P were estimated in the supernatant solution. Surface P was calculated using the equation

$$\text{Surface P} = \frac{B\ (1-y)}{y}$$

Where

B = Amount of P added to the soil

$$y = \frac{\text{Specific activity of equilibrium P solution}}{\text{Specific activity of the original P solution}}$$

b. Chemical Extractable P: Modified Truog's reagent (Ayers and Hagihara, 1952) was used for extracting P from the Hawaiian soils, except the Lualualei. Two grams of soil was placed in 500 ml Erlenmeyer flasks and 200 ml of the extracting solution (0.02N H_2SO_4 + 3 g of $(NH_4)_2SO_4$ per liter) was added. The suspensions were shaken for 30 minutes, centrifuged and P was estimated in the clear solution.

Olsens (1954) sodium bicarbonate method, as described by Chapman and Pratt (1961) was followed to determine extractable P in the Black soils of India and the Lualualei soil.

c. Soil pH Determinations: Soil pH was determined in water paste and paste prepared with 1 N KCl solution. Delta pH was calculated as given below.

$$\Delta\ pH = pH_{Kcl} - pH_{H_2O}$$

Since the soil : P solution ratio used in the adsorption studies

was 1:20, pH was also determined on suspensions of this ratio both with water and 0.01 M $CaCl_2$ solution.

2. Equilibration Time Studies

Three soils, Lualualei, Wahiawa and Akaka were chosen to determine the time required for soils to reach equilibrium with P solutions. One and a half gram soil samples of < 1 mm size were introduced into 50 ml centrifuge tubes, and 30 ml portions of P solutions as calcium phosphate dissolved in 0.01 M $CaCl_2$ were pipetted in. Thus unless otherwise stated, the soil solution ratio was 1:20 in all experiments. The initial P concentrations of the solutions were 35, 70 and 425 ppm for the Lualualei, Wahiawa and Akaka soils respectively. Two drops of toluene were added to each tube. The suspensions were shaken twice daily for 30 minutes each. Samples were removed after at time 1, 2, 4, 6, 8 and 10 days. They were centrifuged at 15,000 rpm for 15 minutes in a temperature controlled centrifuge. Floating organic matters were filtered out using no. 42 paper.

3. Effect of Salt Concentrations on P Adsorption

Three soils, Indian Black soil (Coimbatore), Wahiawa and Akaka were used to study the influence of cations (K or Ca) and salt concentrations on the P remaining in solution. Chloride salt solutions of K and Ca at 0.1, 0.01, 0.001 and < 0.001 M concentrations were used. Potassium dihydrogen phosphate and $Ca(H_2PO_4)_2$ were dissolved in KCl and $CaCl_2$ solutions respectively. The soils were equilibrated for six days after which period pH, P, K and Ca were estimated in the supernatant solutions.

4. Effect of P Adsorption on the Release of Other Inorganic Anions (Hydroxyl, Sulfate and Silicate)

Lualualei, Wahiawa and Akaka soils were selected to study the effect of P adsorption on the release of OH^-, $SO_4^=$ and Si. Distilled water containing increasing amounts of KH_2PO_4 was used for equilibration. In order to have the pH values more meaningful, the equilibration time was reduced to 12 hours continuous shaking. Along with P, pH, $SO_4^=$ and Si were determined in the supernatant solutions.

5. Adsorption Isotherms and Calculation of P Adsorption Maximum Using the Langmuir Equation

Data for plotting sorption isotherms were obtained by equilibrating 1.5 g soil with 30 ml of P solutions for 8 days in the case of Lualualei and Black soils and 6 days in the rest of the soils. Graded amounts of either KH_2PO_4 dissolved in water or $Ca(H_2PO_4)_2$ dissolved in 0.01 M $CaCl_2$ were used as equilibrating solutions. The temperature maintained was approximately 25°C.

For calculating the P adsorption maximum the Langmuir equation was used with some modifications as applicable for solid solution phase. The Langmuir equation can be written in the linear form as below

$$\frac{C}{x/m} = \frac{1}{Ab} + \frac{C}{b}$$

Where

C = P remaining in solution (μg.P/ml)

x/m = P adsorbed by the soil (μg.P/g)

b = Adsorption maximum

A = Constant related to bonding strength

P adsorption data were plotted with C on the absicca and $\frac{C}{x/m}$ on the ordinate. The reciprocal of the slope was calculated to obtain the P adsorption maximum.

6. Determination of "Equilibrium Phosphate Potential"

Five g soil samples were shaken for 30 minutes with 50 ml portions of 0.01 M $CaCl_2$ solution containing increasing amounts of P as calcium phosphate. The suspensions were then centrifuged and pH, Ca and P were determined in the supernatant. A brief calculation procedure for getting the phosphate potential is given below. For a detailed account the reader is referred to the report of Aslyng (1954).

$$\text{Phosphate Potential} = 1/2\ pCa + pH_2PO_4$$

$$1/2\ pCa = -1/2\ (\text{Log}_{10}\text{Con.}_{Ca} + \text{Log}_{10}\gamma Ca)$$

(activity coefficient was calculated using Debye Huckel equation.

$$\gamma = \frac{-AZ^2\sqrt{S}}{1+ab\sqrt{S}}$$

Where

A = 0.5

Z = Valency of cation (2)

S = The ionic strength ($1/2\ \Sigma\ mZ^2$)

aB = 1.5

Activity of $H_2PO_4^-$ was calculated after applying the correction factor derived by Aslyng (1954) relating H_2PO_4/P, to pH.

"Equilibrium phosphate potential" was arrived at by plotting P adsorbed (+ΔP) or desorbed (-ΔP) vs phosphate potential, and taking the potential value at ΔP = 0.

7. Effect of Temperature on P Adsorption and Calculation of "isosteric" heat of Adsorption

To calculate isosteric heat of adsorption ($\overline{\Delta H}_{x/m}$) the P adsorption isotherms were constructed at 10, 25 and 35°C for Molokai and Red Soil (Coimbatore) and at 10, 20 and 30°C as for Wahiawa. Since the adsorption data when plotted as 1/T vs log C remaining in solution, formed a near to perfect straight line (r = 0.99) in these soils, only two temperatures, 10 and 25°C, were tried in the rest.

For the above study 2 grams soils were taken in 125 ml Erlenmeyer flasks. Mono calcium phosphate dissolved in 0.01 M $CaCl_2$ solution were brought to five degrees less than the appropriate T. Forty ml of these solutions were pipetted in and after adding two drops of toluene the flasks were dipped to neck level in a temperature controlled water bath. The suspensions were well stirred frequently during the equilibration period of 6 or 8 days depending on the soils. The temperature control was ± 0.1°C. After centrifuging the suspensions in a temperature controlled centrifuge, the P was estimated in the supernatant.

Wherever the isotherm data for three temperatures were available, isosteric heat of adsorption was calculated by plotting log C (P remaining in solution) against 1/T, at different amounts of P adsorbed, and by multiplying the slope of the straight line by 2.3 R.

Where the data involved only two temperatures a direct application of the ~~equation~~ the following equation was used.

$$-\overline{\Delta H}_{x/m} = \text{Log } \frac{C_2}{C_1} \cdot \frac{2.3 \text{ R } T_1 \text{ } T_2}{T_2 - T_1}$$

Where

$\overline{\Delta H}_{x/m}$ = Isosteric heat of adsorption KCal Mole^{-1}

T_1 = Lower temperature (in absolute scale)

T_2 = Higher T

C_1 C_2 = P concentration in solution at T_1 and T_2 respectively

R = Gas constant (1.987 KCal mole^{-1})

8. Phosphate Desorption Isotherms

The Lualualei, Wahiawa and Akaka soils were used for desorption studies. For each soil 20 samples weighing 1.5 g were introduced into 20 weighed centrifuge tubes. Following the procedure for the adsorption experiment, the equilibrium P concentration was raised to about 10 ppm. The samples were then transferred to appropriate containers of different sizes, and various amounts of $CaCl_2$ solutions were added to give a soil : solution ratio 1:20 to 1:400 in Lualualei and Wahiawa soils and up to 1:650 in Akaka soil. The samples were shaken for 4 hours and P was estimated in the equilibrated solution. The amount of P desorbed was calculated and subtraction of this from the adsorbed P, enabled construction of P desorption isotherms.

Greenhouse Experiment

1. General

The Greenhouse study was conducted with the following objectives.

i) To find out the adjusted solution P concentration required in different soils for near maximum crop yield. ii) To study the relationship between the P adsorption maximum, calculated using the Langmuir equation, and crop yields and P uptake. iii) To determine the L value of the soils when different amounts of carrier P were applied with P^{32}. iv) To compare P response curves of a monocot and a dicot.

Eight Hawaiian and four Indian soils were chosen for the first three objectives. They were Lualualei, Molokai, Wahiawa, Kapaa, Maile, Hanipoe, Naalehu and Akaka soils from Hawaii, and Black Soil (Coimbatore), Red Soil (Coimbatore), Low Level Laterite (Vallam) and High Level Laterite (Doddabedda) from India. Pearl millet (Pennisetum typhoides) was grown in these soils. A randomized complete block design was adopted with two replications.

For the fourth objective, another experiment was set up with the Lualualei, Wahiawa and Akaka soils. A legume, Desmodium intortum, was grown. The experimental design was the same as for millet.

Six hundred grams of oven dry soil was used for growing millet and desmodium. For selecting the P treatments, the adsorption data obtained following the standard procedure (0.01 M $CaCl_2$ + Ca $(H_2PO_4)_2$ ionic environment, 6 days or 8 days equilibration and room T) were plotted with P adsorbed against log C. Solution concentrations of 0.022, 0.066, 0.2, 0.6 and 1.8 ppm were chosen and the amounts of P required were calculated by intercepting the Y axis at the pertinent solution P concentrations. The P requirement was then corrected for the 2 mm fraction of the soil in the potculture trial.

For determining L values, calculated amounts of radioactive P were

mixed with P fertilizer at treatments of 0.022, 0.066 and 0.2 ppm P.

2. Fertilizer Application and Potting Procedure

Before applying the fertilizers, the soils were moistened with distilled water just enough, not to immediately hold tightly the nutrients, especially the P, and at the same time easy to work with. The quantity of water added was roughly 40 % of the water holding capacity. The amount was kept constant within the same soil. The soil was spread to a thin layer on aluminum trays covered with polythene sheet. Blanket application was done first. Each soil received 200 ppm N as calcium nitrate, 200 ppm K as potassium chloride, 50 ppm Mg as magnesium sulfate, 25 ppm Zn as zinc acetate, 5 ppm Cu as copper chloride and 1 ppm B as boric acid. The soil was mixed well and was spread again. Phosphorus was applied as phosphoric acid, in the form of fine spray under 7 lb pressure, using an atomizer. After a thorough mixing the soils were put into polythene bags and left to equilibrate for 15 days, during which period mixing was done in the alternate days. At the last mixing, to make the volume of soils for plant growth comparable perlite was added to soils of smaller volume, and then the soils were potted in weighed tin cans.

3. Planting and Further Operations

Twenty pre-germinated millet seeds were sown in each pot and the moisture level was maintained at water holding capacity, by weighing the cans every day and irrigating with distilled water. When the plants were about 5 cm high, the number was thinned down to 10 plants per pot. In the case of the Low Level Laterite, Red Soil and High Level Laterite,

$Ca(OH)_2$ equivalent to twice the amount of exchangeable aluminum was added.

As the growth rate of millet varied highly between soils, to avoid pot bound condition of roots in some soils, it was decided to harvest the plants when the maximum height reached 30 cm. On harvest the plants were washed once with distilled water and dried in an air oven at 85°C. After taking the dry weight the plant samples were ground and stored for P analysis.

In the case of desmodium, the same fertilizer application and potting procedures were followed as for millet. Before sowing, the seeds were scarified with concentrated H_2SO_4 to facilitate easy germination. Forty seeds were sown and after a week only 25 plants were maintained. Harvesting was done when the fourth pair of leaves started unfolding.

Analytical Procedures

The clay minerals of Indian soils were identified by X-ray diffraction and differential thermal analysis.

Water saturation extracts were obtained following the procedure described in the Agricultural Handbook No. 60, U.S.D.A. (1969).

Phosphates in soil solutions were determined by the molybdenum blue method using $SnCl_2$ in H_2SO_4 or HCl as the reducing agent, depending on the sensitivity requirement (Chapman and Pratt, 1961, pp. 62, 170).

Silico-molybdate blue complex method of Kilmer (1965) was followed for silicon determination.

Calcium was estimated by titration with EDTA, and using atomic

absorption spectrophotometer, in the water saturation extract and for phosphate potential calculations respectively.

Sulfate was determined following the turbidimetric procedure of Bardsley and Lancaster (1960) as modified by Fox, et al. (1964).

Plant Analysis and Calculation of L Values

The powdered plant samples were wet digested in nitric perchloric acid medium and the volume was made up to 50 ml. Aliquots from these were taken and P was determined colorimetrically by Vandate Molybdate-Yellow method using Barton's reagent (Kitson and Mellon, 1944).

For radio-active assay one or two ml of the samples were taken in stainless steel planchets. After neutralizing the acid with ammonia, the solution was evaporated and counting was done using a thin window GM counter. L value was calculated using the same equation as for surface P except that the Y here represents the fraction of fertilizer P in the plant, obtained by dividing specific activity of the sample solution by the specific activity of the applied P fertilizer solution.

RESULTS AND DISCUSSION

Effect of Equilibration Time on P Sorption

Lualualei, Wahiawa and Akaka soils were used to study the influence of duration of equilibration on P sorption. Fractional rates of P sorption as a function of time are plotted in Figure 2. The change in solution P concentration with time is illustrated in Figure 3. Most of the P was adsorbed within 24 hours. However, P removal from the solution continued up to 6 days in all the soils studied. Similar observations indicating slow attainment of phosphate equilibria by Hawaiian soils have been reported earlier by Davis (1935), Fox, et al. (1968, 1970). However, investigators elsewhere have concluded that equilibrium was essentially complete in 1-3 days.

The time required for solution P to reach equilibrium with the solid phase depends on i) the nature of P-reactive sites, ii) size of the soil particles, iii) stability of the aggregates, and iv) P concentration in solution. Highly reactive surfaces, small particle size and water unstable aggregates should be associated with rapid reaction. Equilibrium may be reached quickly when the P concentration of the solution is low. Sometimes this could be due to the limitations of one of the reactants, the adsorbate itself. The relative rates of P sorption (Fig. 2) show that for 99 % adsorption 4, 6 and 8 days were required for Akaka, Wahiawa and Lualualei soils respectively. Probably this was more related to the nature of reactive sites than the other factors enumerated. Thus Akaka developed under high rain-fall conditions contains more highly reactive "hydroxo" groups resulting in faster kinetics of reaction as compared with "oxo" groups which dominate the Wahiawa soil, formed under

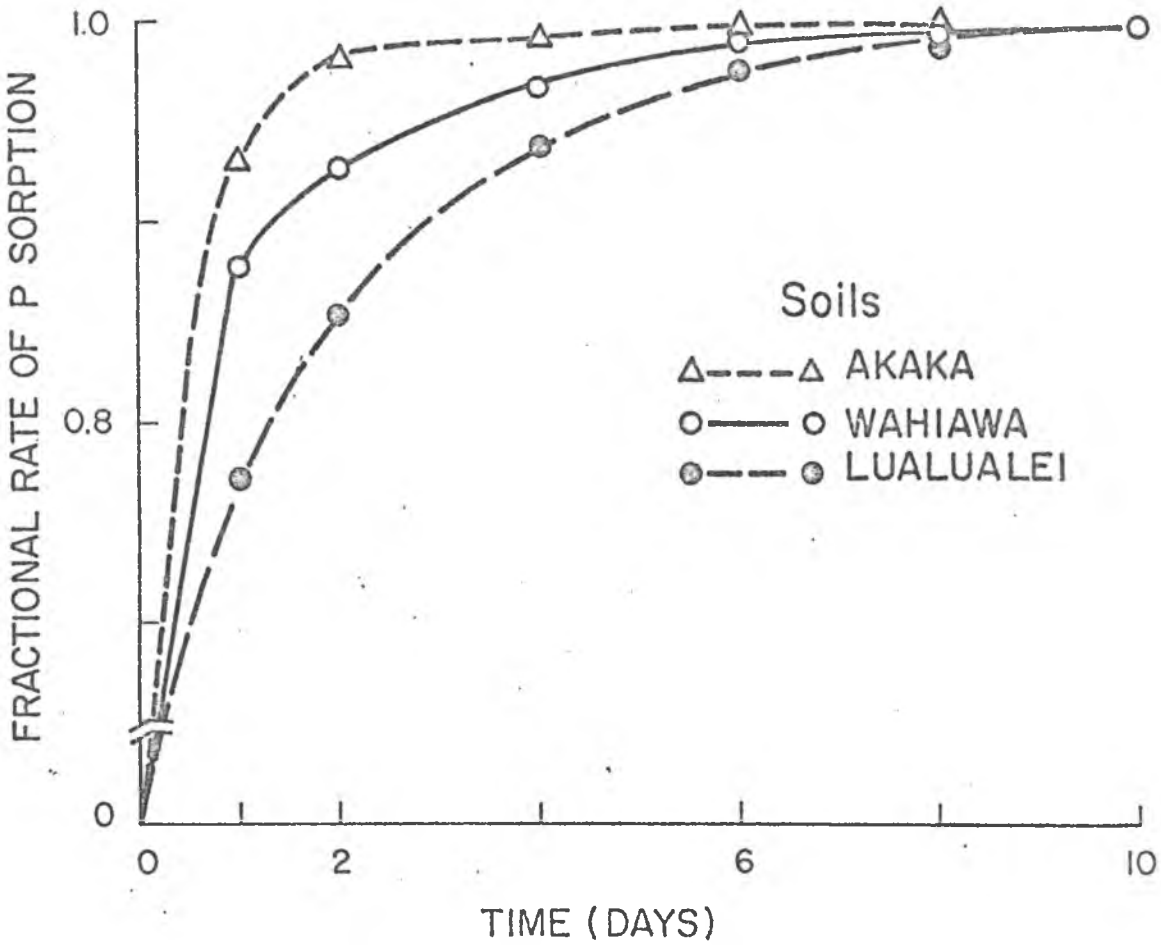


Fig. 2-Rate of P sorption by three Hawaiian soils as a function of time (Medium - 0.01 M $CaCl_2$+$Ca(H_2PO_4)_2$

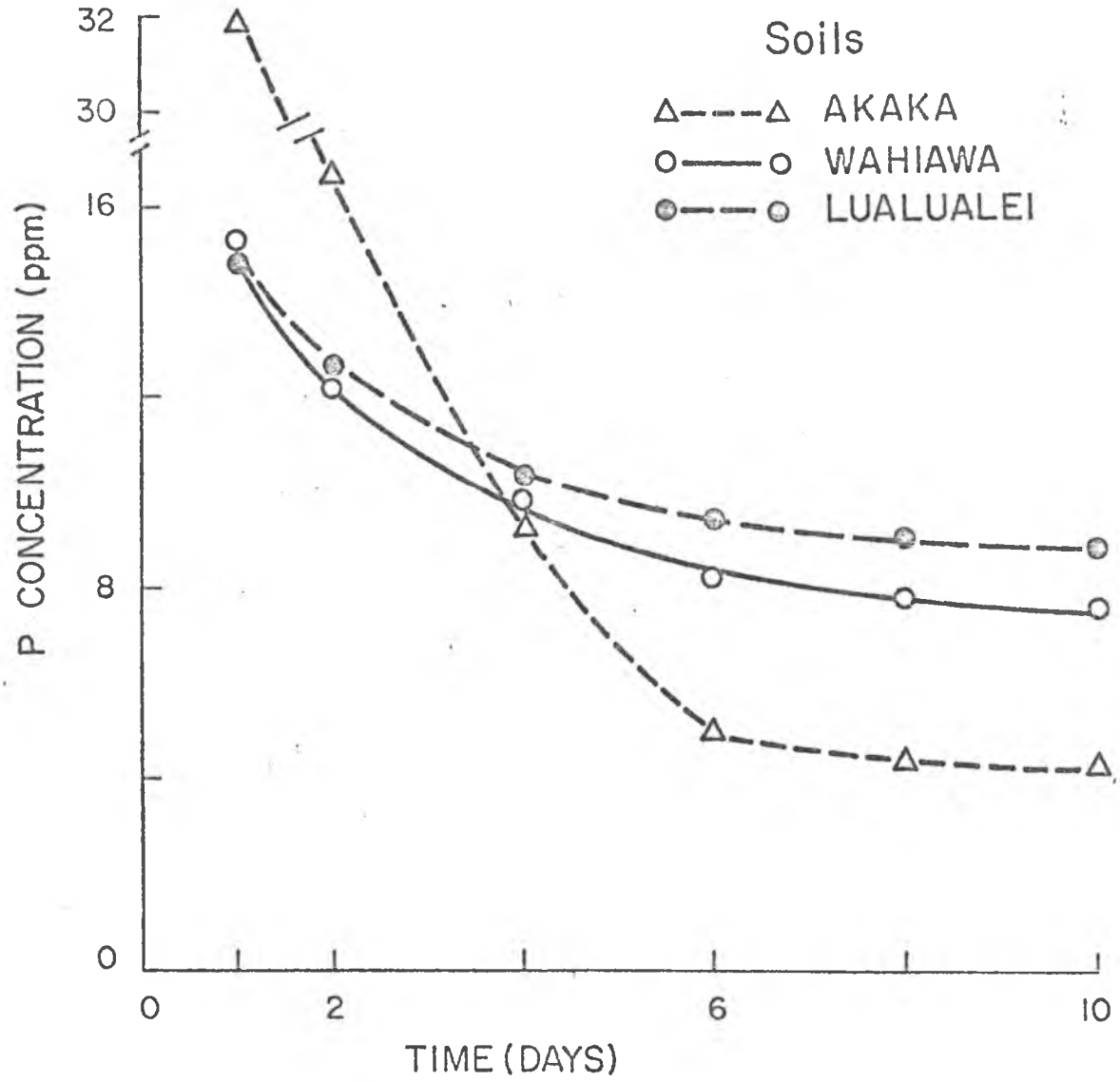


Fig. 3-Phosphorus remaining in solution in relation to reaction time

Initial P conc: Lua 35
Wahi 70
Ki 425

conditions of less intense weathering. The peculiar behavior of Lualualei can be ascribed to a different mechanism of P retention, associated with an abundance of calcium salts whereas retention of P by latosols was associated with hydroxides and oxides of iron and aluminum.

Although periods of less than 12 hours have been used for some phosphate studies (Low and Black, 1950; Rennie and McKercher, 1959), the present study shows that reducing the reaction period from 6 days to 12 hours shifts the P sorption isotherms considerably. This results in a reduction of adsorption maxima, as calculated using the Langmuir equation, in some cases to the extent of 31 % (Fig. 4).

Influence of Ionic Environment on P Sorption

Three variables, soil, salt concentration and type of cation were incorporated in this part of the study on P sorption. The results are illustrated in Figure 5. For easy comparison of soils, the same data are plotted in Figure 6. However, the ordinate here represents the increase in P sorption, calculated by subtracting the adsorption value obtained when $Ca(H_2PO_4)_2$ or KH_2PO_4 were used without either $CaCl_2$ or KCl. The results show an increase in P sorption with increase in the ionic strength of both $CaCl_2$ and KCl. In general the magnitude of increase is high at the low range of salt concentration.

Let us now compare the soils in relation to salt effects on P sorption. Figure 7 shows that the increase in P sorption with increase in the ionic strength of KCl is the greatest for Akaka soil followed by Wahiawa and Black Soil. However, a different trend was obtained when $CaCl_2$ was used. The order of influence of increase in $CaCl_2$ concentration on P sorption increase arranged according to the soils are Wahiawa >

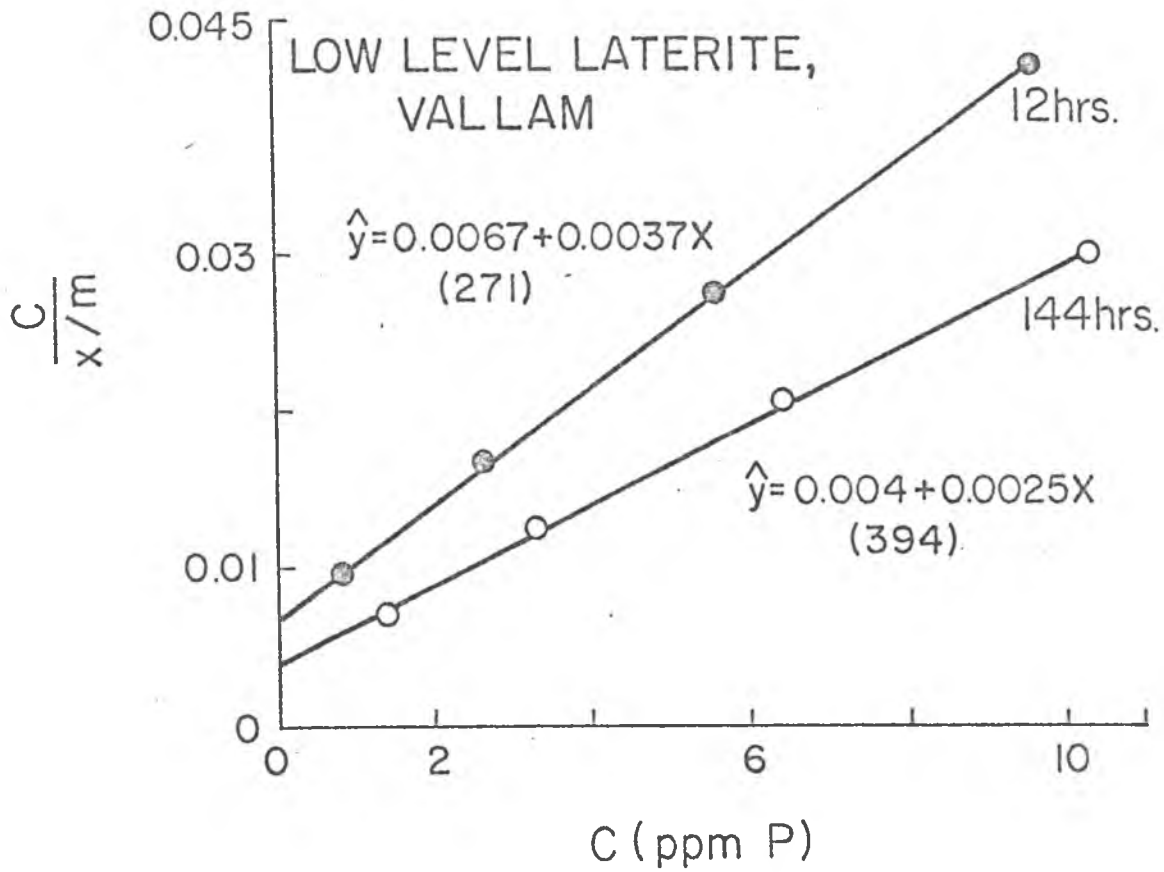


Fig. 4-Effect of time on the slopes of the Langmuir plot of P sorption isotherm of a Low Level Laterite soil (0.01 M $CaCl_2$ medium. Values in parentheses are calculated adsorption maxima).

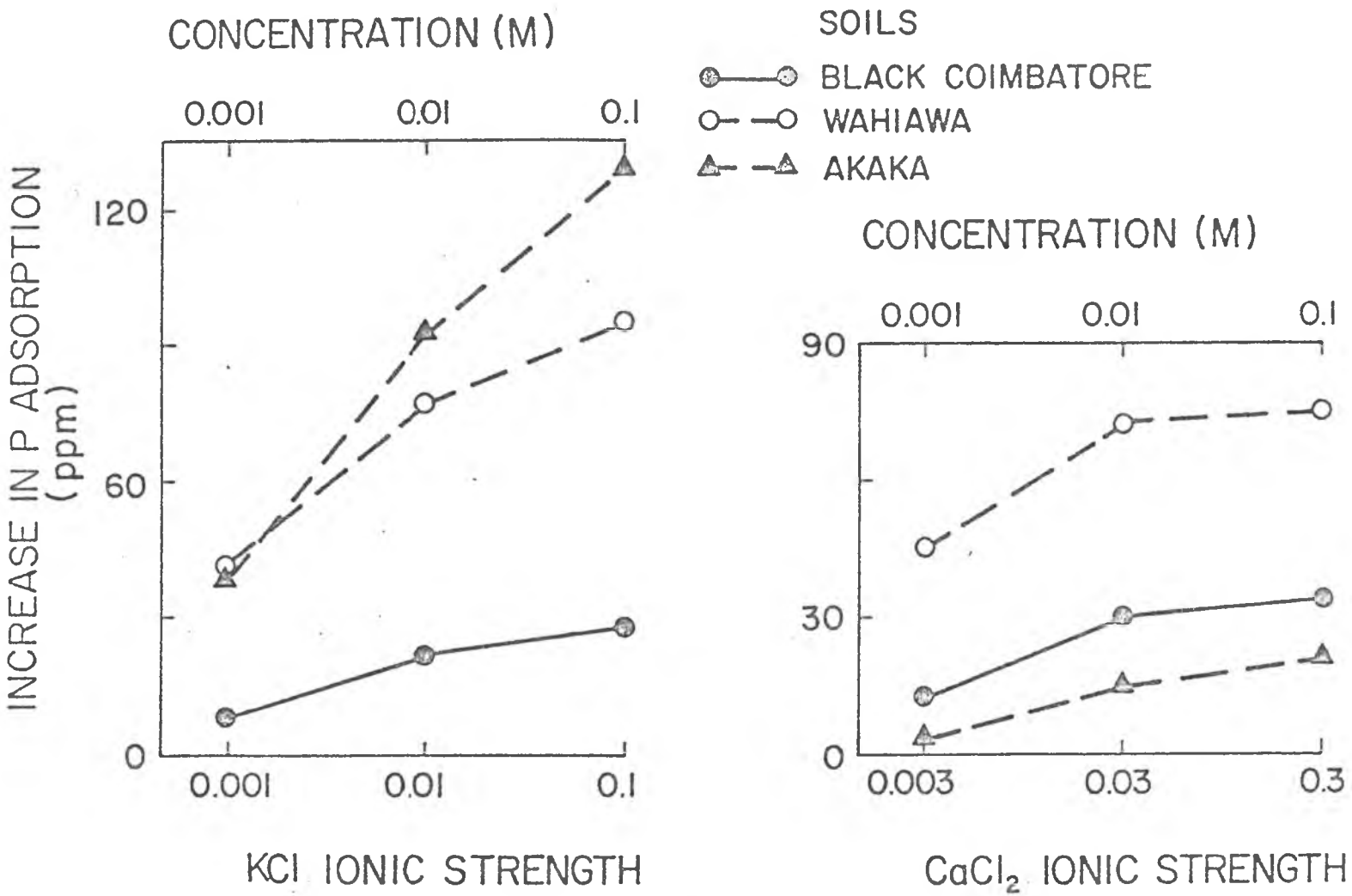


Fig. 6-Increase in P adsorption by three soils effected by KCl or $CaCl_2$ addition to the equilibrating solution plotted against the ionic strengths and concentrations of KCl and $CaCl_2$

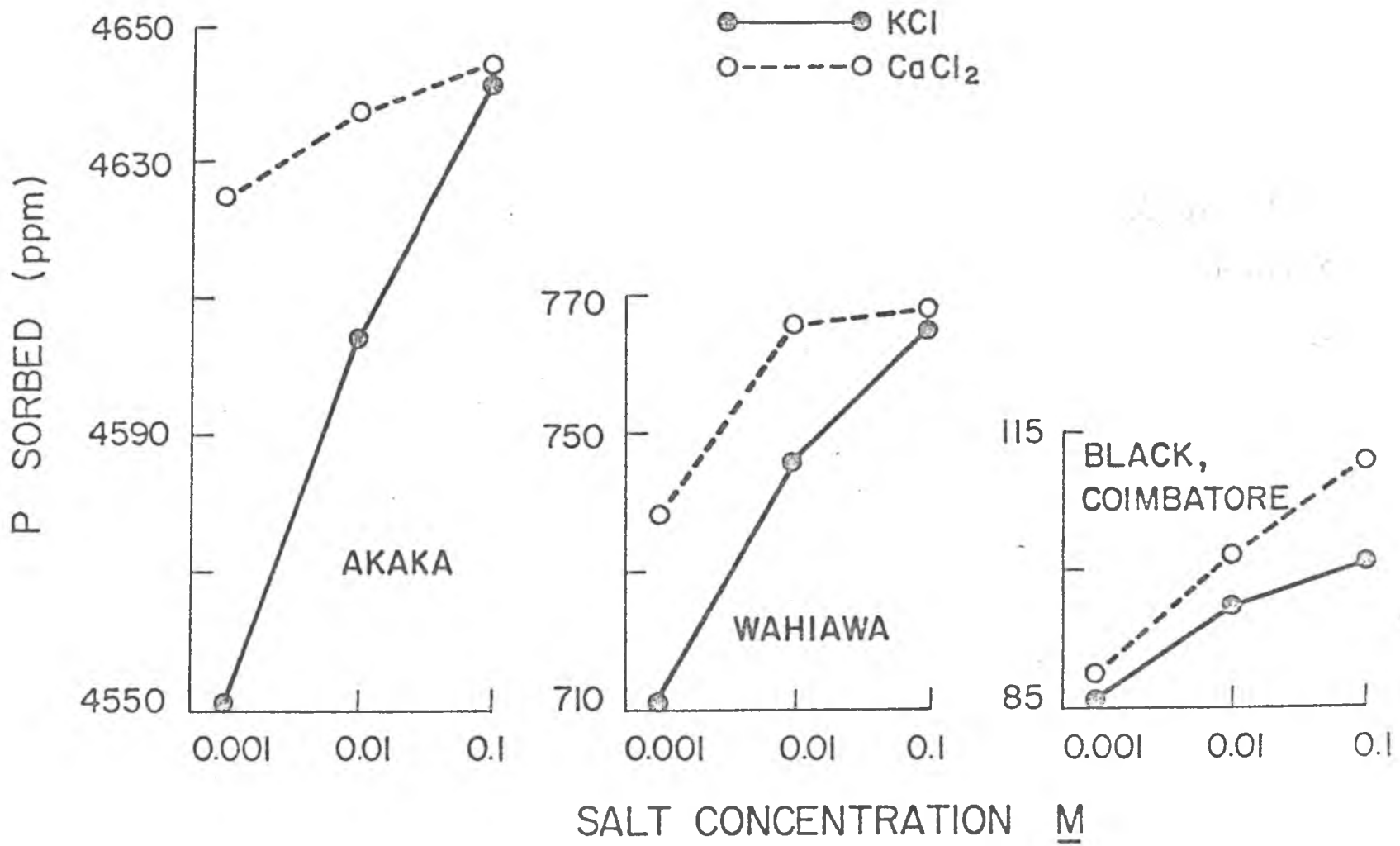


Fig. 7-Influence of cations (Ca & K) and salt concentrations ($CaCl_2$ & KCl) on P adsorption by three soils (6 days equilibration)

Black Soil > Akaka. Turning our attention to comparing the cation effects, the presence of calcium resulted in enhanced P sorption by all the soils. The magnitude of increase was highest for Akaka followed by Wahiawa and Black Soil, Coimbatore. Of the soils used, Akaka was influenced most by increasing the ionic strength of KCl and by replacing K with Ca ions. Since P sorption by the Akaka soil was greatly increased even when small amounts of calcium were present in solution, a further increase in calcium did not enhance P adsorption as much as for other soils.

As reviewed in the Literature Section, many researchers have noted salt effects on P adsorption by soils. Increased P adsorption can be attributed to pH effects and co-adsorption of P with the cations. In soils like Akaka where the solids have constant potential surface, both reasons may account for high adsorption. However, in cases like the Black Soils (constant charge surface), co-adsorption is likely to play a dominant role. As can be seen in Table 4, for all the soils pH decreased with increasing salt concentration. This generalization is in keeping with previous reports of Chao, et al. (1965) and Mekaru (1969).

The amounts of Ca, K and P adsorbed by soils at different salt concentrations are summarized in Appendix Table 1. As one would expect, increasing cation concentrations resulted in higher adsorption. It is possible that adsorbed polyvalent cations were sources of positive charges for P adsorption.

The slope of the Langmuir P adsorption plot was considerably different for different salt media (Fig. 8). Table 5 gives an idea of the magnitude of variation in adsorption maximum due to different ionic

Table 4. Effect of salt concentrations and cations (Ca & K) on the pH of Black Soil, Coimbatore, Wahiawa and Akaka soils. Soil:Solution Ratio 1:20. The solution pH values are given for comparison.

Salt	Concentrations M/Liter	pH			
		Solution	Black Soil	Wahiawa	Akaka
$CaCl_2$	0.001	4.90	7.71	5.32	4.05
	0.010	4.87	7.26	5.07	4.05
	0.100	5.65	6.70	4.78	3.98
KCl	0.001	5.00	8.21	5.73	4.31
	0.010	5.00	7.59	5.20	4.28
	0.100	6.15	7.30	5.19	4.30

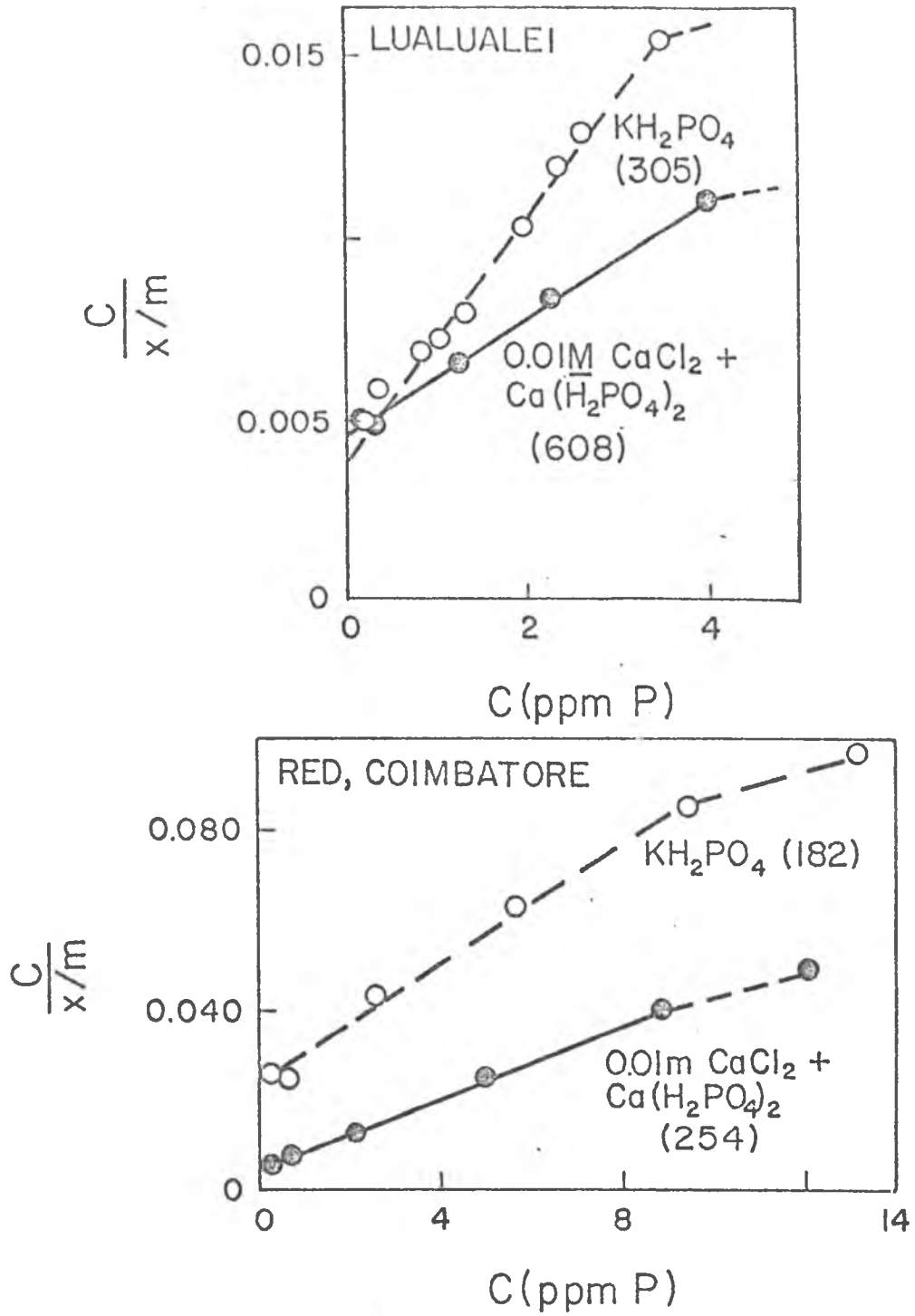


Fig. 8-The Langmuir plot of P sorption isotherms as affected by the ionic environment (values in parentheses are calculated adsorption maxima)

Table 5. Influence of ionic environments on phosphate adsorption maxima of soils calculated with the Langmuir Equation[a]

Soil	Adsorption Maximum (ppm)	
	KH_2PO_4 in H_2O	0.01 M $CaCl_2$ + $Ca(H_2PO_4)_2$
Lualualei	305	608
W!hiawa	666	861
Red Soil, Coimbatore	181	241
Red Soil, SVRP	60	127
Low Level Laterite, Pallathur	152	416

[a]Equilibration time - Lualualei 8 days
Others 6 days

environments. This suggests that it is imperative that one describe equilibrating media when reporting results based on P sorption isotherm. Although many workers have used 0.01 M $CaCl_2$ for constructing P sorption isotherms, it has the analytical disadvantage of low equilibrium concentrations of P in solution. Schofield (1955) originally proposed using this concentration as an approximation to the calcium content of the soil solutions. However, water saturation extracts of the soils used here never exceeded 0.005 M Ca (Table 6). A more realistic concentration of calcium chloride seems to be 0.005 M. This still has the advantages of a clear extract and more accurate P estimations. Nevertheless, 0.01 M $CaCl_2$ was used in the present study, although 0.005 M $CaCl_2$ media is recommended for future studies.

Phosphorus Sorption Isotherms

P adsorption by non-calcareous soils. All the soils from Hawaii and India were used in this study except the Lualualei and Black soils. The most highly weathered Hawaii Latosols contain crystalline and/or amorphous iron and aluminum hydrous oxides which persist as end products of weathering. The dominant clays of the Molokai and Wahiawa soils are kaolinites, whereas x-ray amorphous materials are abundant in Maile, Hanipoe, Naalehu and Akaka. All these soils show moderate to strong acid reaction in water paste. Only the Akaka soil has a net positive charge as indicated by a positive delta pH (Table 3).

Regarding the Indian soils, the Red and Low Level Laterite soils mostly contain kaolinite in the clay fraction. Kaolinite mineral and gibbsite dominate the colloidal fraction of the High Level Laterite soils. All the Indian soils have a net negative charge (Table 3).

Table 6. Concentration of calcium in the water saturation extract of 8 Hawaiian and 4 Indian soils (12 hours equilibration time)

Soil	Calcium (M/liter)
Hawaiian Soils	
Lualualei	0.0008
Molokai	0.0007
Wahiawa	0.0002
Kapaa	0.0007
Akaka	0.0011
Naalehu	0.0050
Maile	0.0016
Hanipoe	0.0007
Indian Soils	
Black Soil, Coimbatore	0.0044
Red Soil, Coimbatore	0.0044
Low Level Laterite, Vallam	0.0008
High Level Laterite, Doddabedda	0.0014

The standard procedure used to gather data for P sorption isotherms presented here involved monocalcium phosphate dissolved in 0.01 M $CaCl_2$ as equilibrating solution and 6 days equilibration time at 25°C (approximate). Potassium phosphate dissolved in water and equilibration periods less than 6 days were used for comparison. The P sorption isotherms of 9 soils, plotted with the phosphate adsorbed against equilibrium solution concentration are presented in Figures 9 to 14. An adsorption isotherm can be defined "as the relationship between the amount of a substance adsorbed by an adsorbant and the equilibrium concentration of the substance at constant temperature" (Prutton and Maron, 1953). Since P removal by soil from solutions of low concentrations, is predominantly adsorption, in the following discussion the more restricted term adsorption is used rather than sorption.

Brunauer (1945) considered five principle forms of isotherms - the shapes being determined by the nature of the reactions either physical or chemical adsorption, relative affinities between the adsorbent and the adsorbate and the number of sites available. The isotherms obtained here resemble the monolayer type in the concentration range, 0 to 10-20 ppm, after which a marked increase in P adsorption is noticed. The shape of the isotherm suggests multilayer adsorption or perhaps reactions in addition to saturation of primary P reactive sites. To facilitate rigorous treatment of the isotherms the portion of the curve before and after the inflection points are treated separately.

As cited in the literature section, one evidence that adsorption is the process of P retention by soils at low P concentrations is resemblance of the isotherm to the characteristic type described by the Langmuir

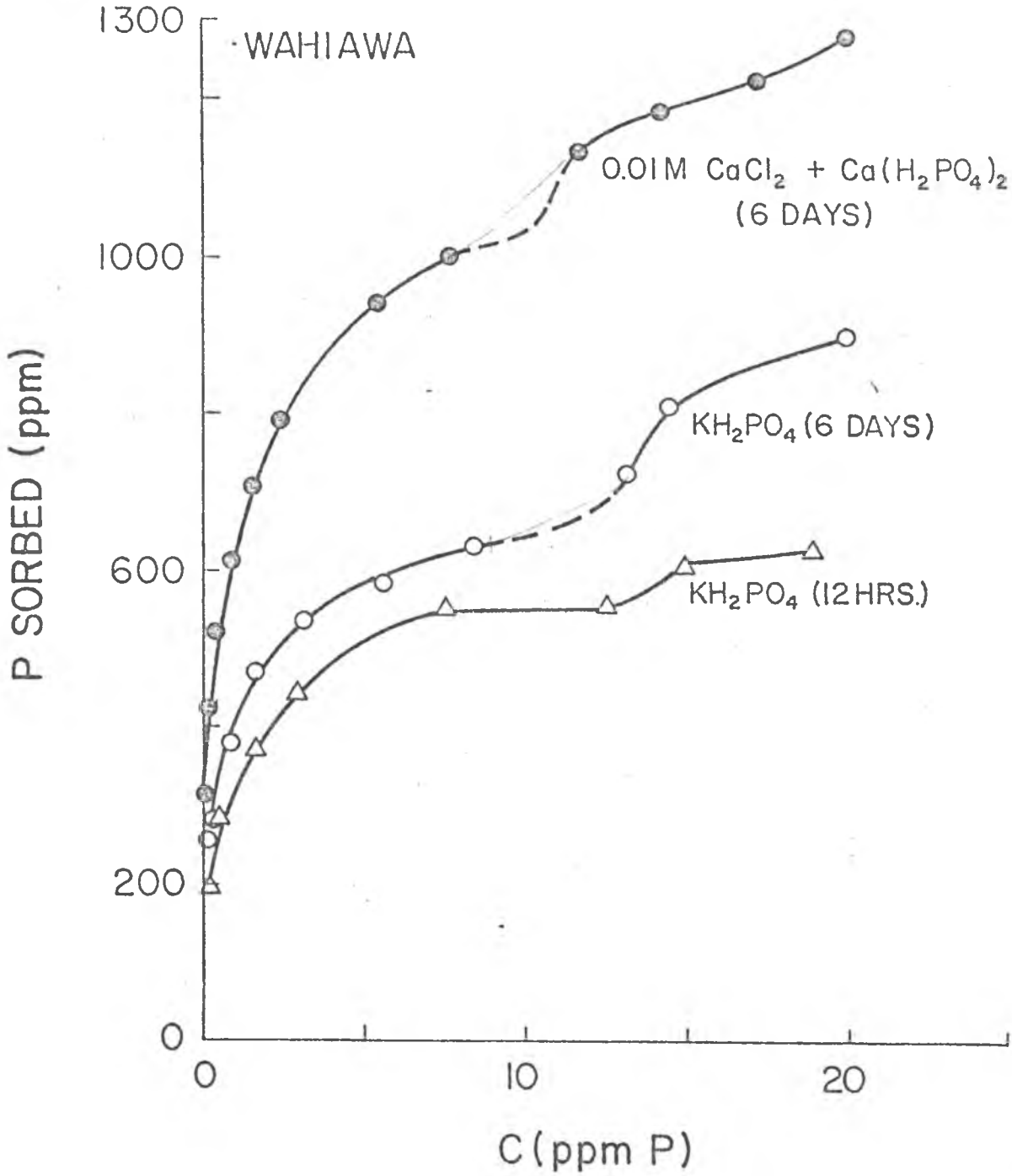


Fig. 9-Characteristic of "humps" on P adsorption isotherms of Wahiawa soil. (C = equilibrium solution concentration of P)

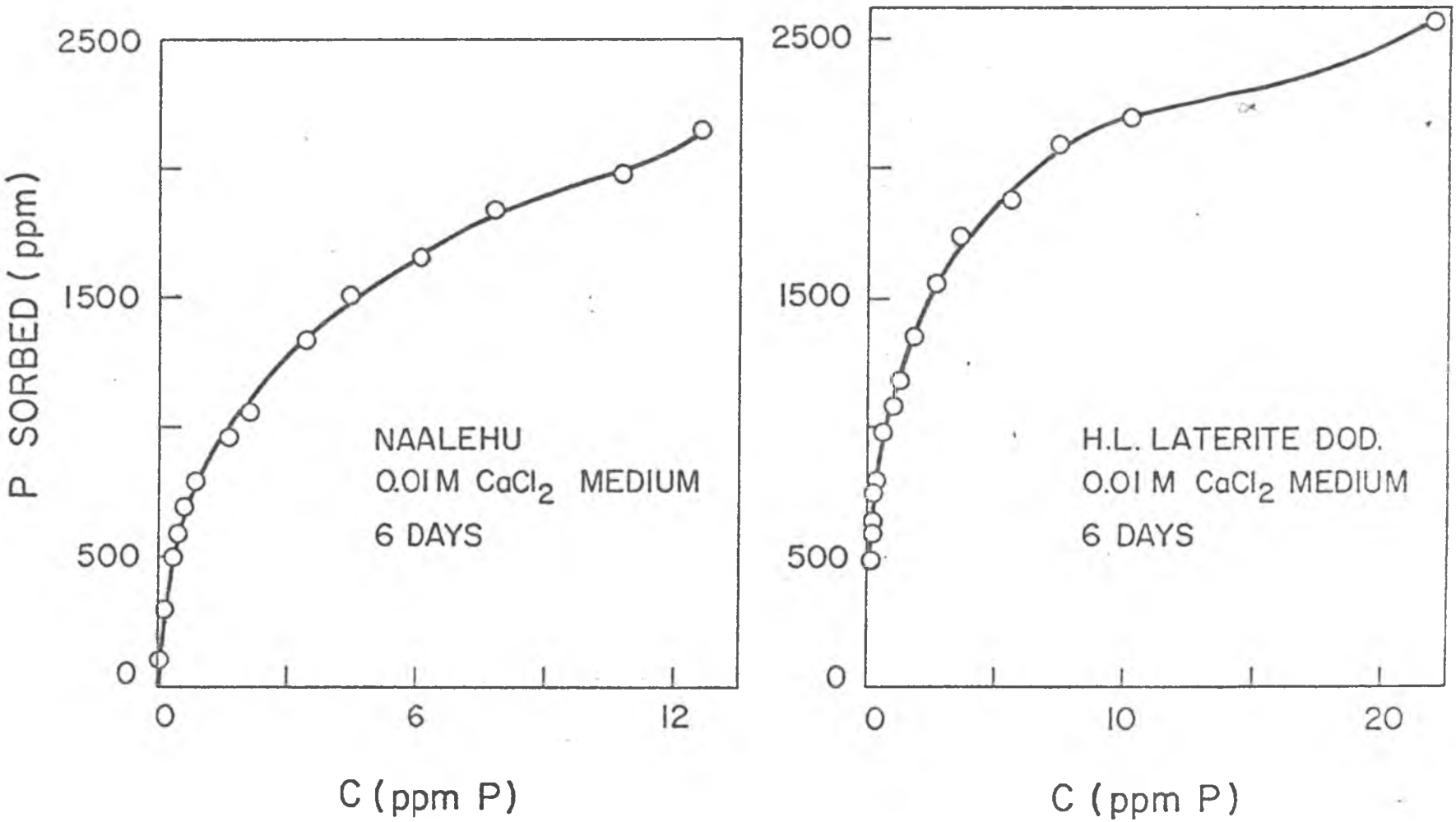


Fig. 10-Phosphorus adsorption isotherms of Naalehu and High Level Laterite soils (Note the tendency for marked increase in P adsorption at high solution P concentrations, C)

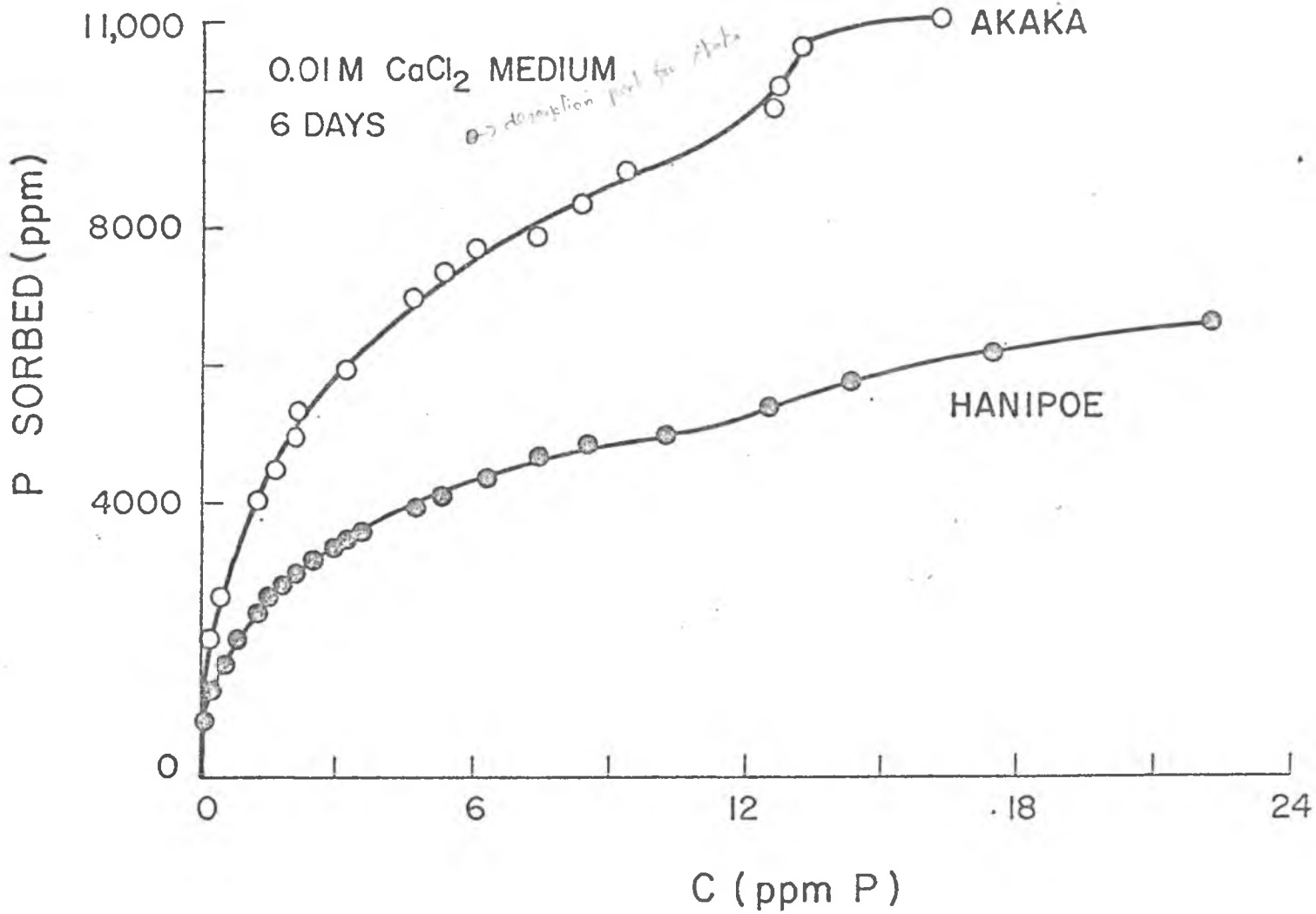


Fig. 11-Phosphorus adsorption isotherms of Akaka and Hanipoe soils
(C = equilibrium solution concentration of P)

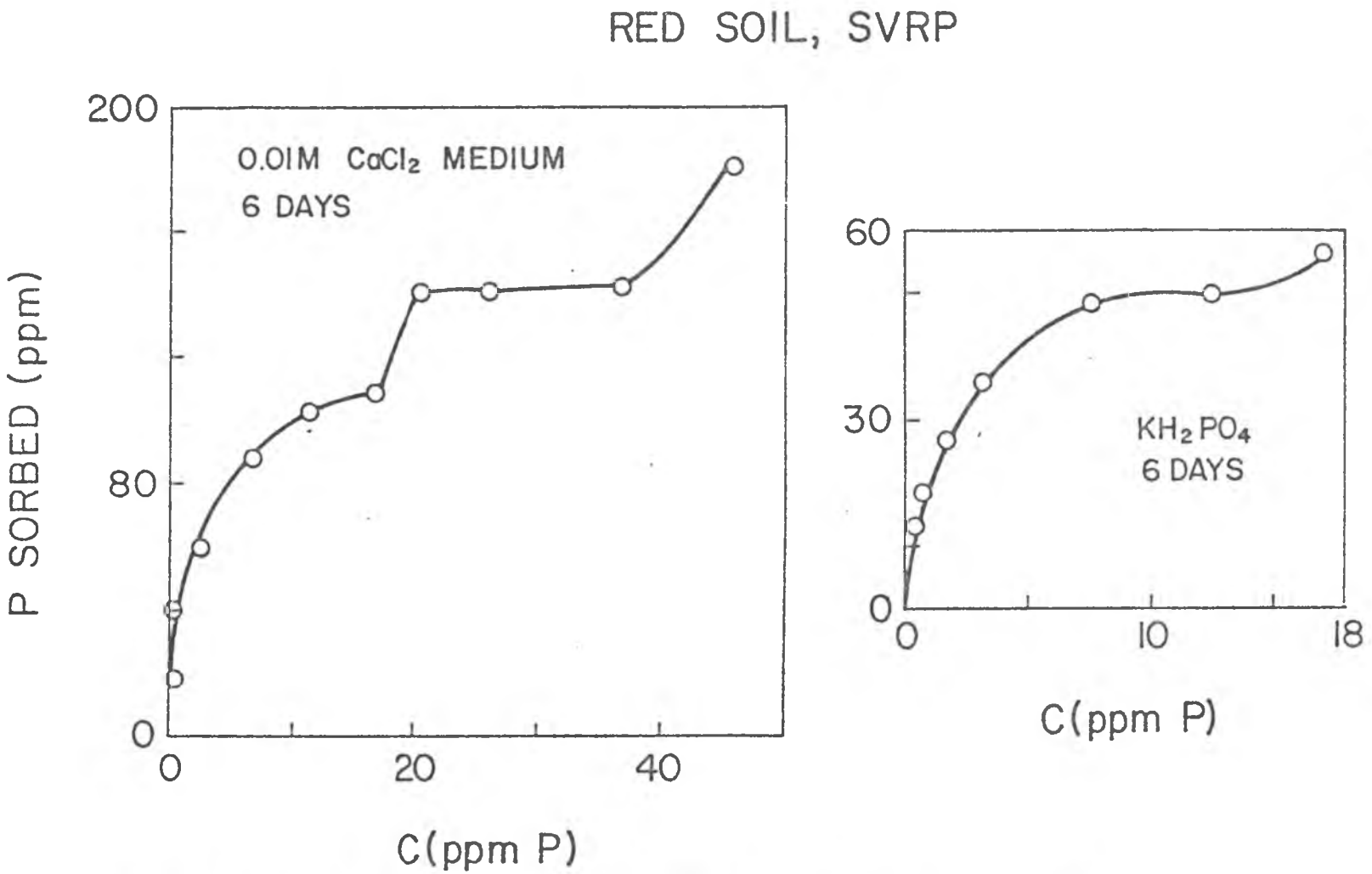


Fig. 12-P adsorption isotherms of Red Soil, SVRP in two salt solutions. (Abrupt increase in P adsorption occurs at approximately 20 and 40 ppm P (C) in $CaCl_2$ medium and 18 ppm in the KH_2PO_4 medium)

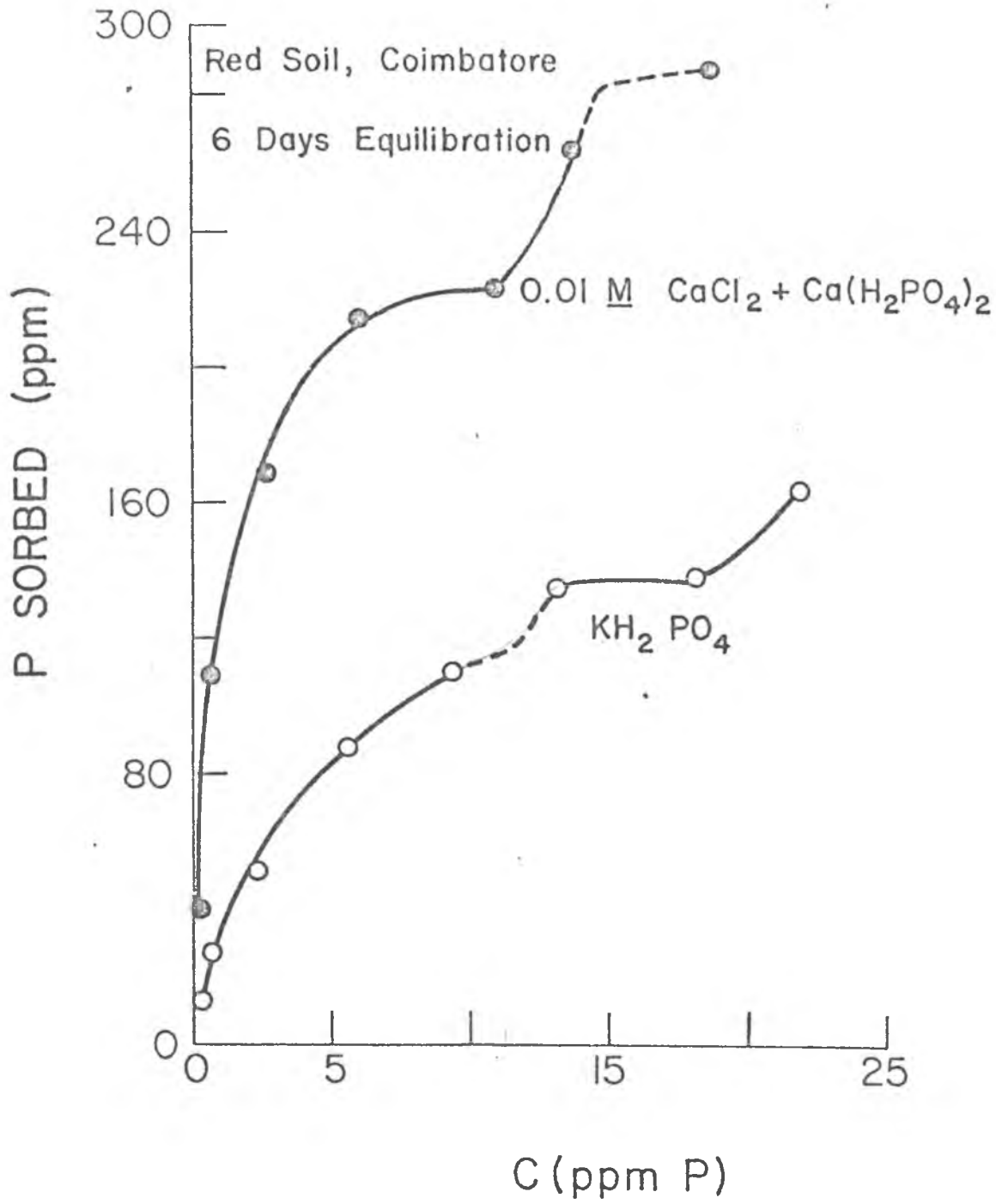


Fig. 13-P adsorption isotherms of Red Soil, Coimbatore in two ionic environments (C is the equilibrium solution concentration of P)

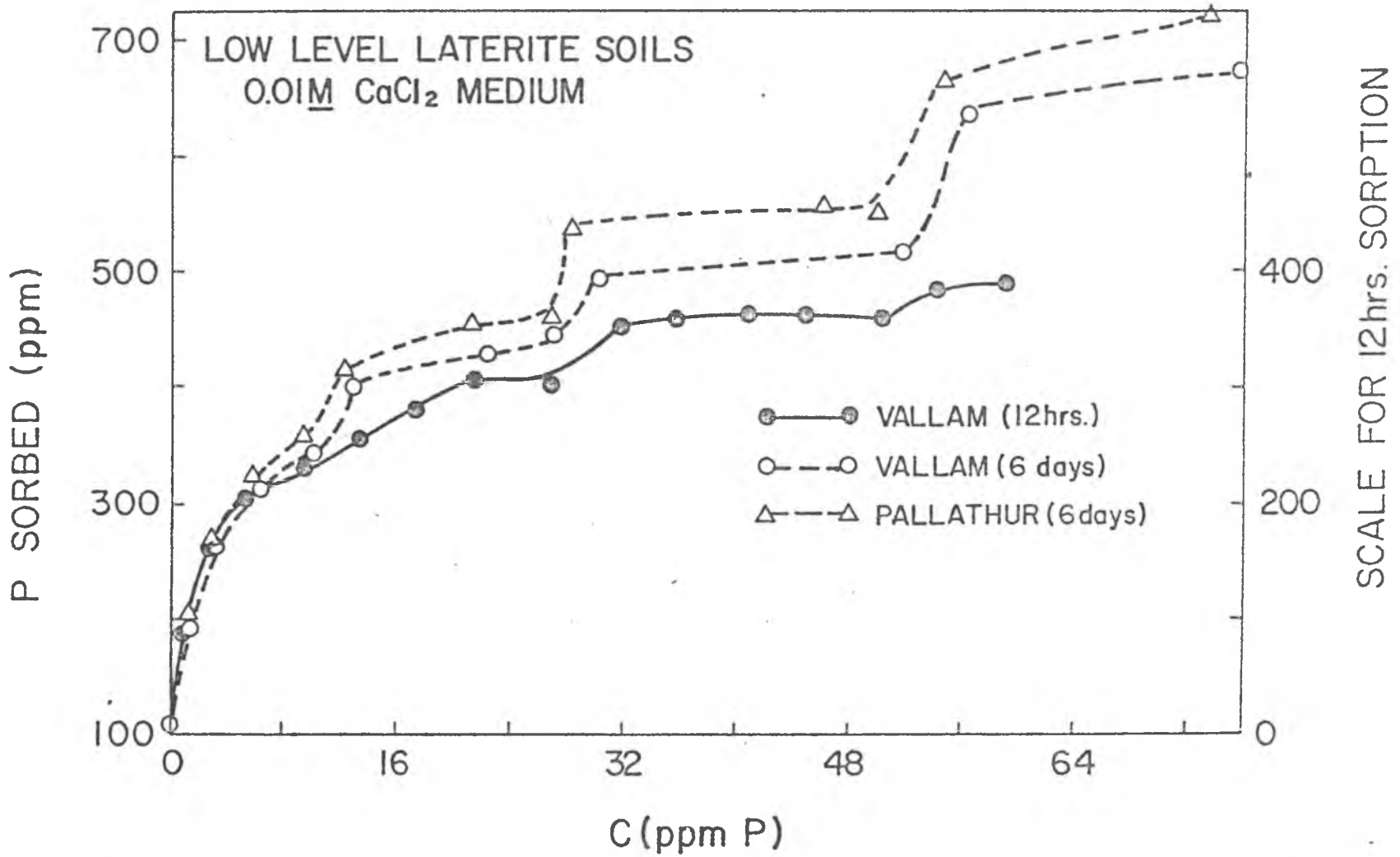


Fig. 14-Three "humps" characterize P adsorption isotherms of two Low Level Laterites from India.

equation. In the present investigation all the soils gave a good fit to the Langmuir equation. This enabled calculation of the adsorption maxima, which corresponds to the saturation of primary P reactive sites. Another method of detecting the same is by observing adsorption corresponding to the "knee" of the curve. If adsorption in the region before the inflection point is dominantly to form a monolayer on P reaction sites, a close agreement could be expected between the calculated (b_{max}) and observed monolayer saturation of P reaction sites. Table 7 summarizes the observed and calculated values for monolayer adsorption. A high correlation coefficient (Figure 15, r = 0.994, n = 21) strongly suggests that the adsorption in this region was mainly the monolayer type and that other reactions were relatively unimportant. In the discussions to follow, the portion of the isotherm before the inflection point will be called "apparent monolayer region."

The apparent monolayer region could be divided into three regions as described below.

Region I. Occurring at equilibrium solution concentrations of < 1 ppm P. The isotherm line remains parallel to Y axis and probably represent very high affinity for P retention.

Region II. The line is convex to Y axis. Occurs at concentrations between 1 to 3.5 ppm.

Region III. The isotherm is still convex to Y axis though the angle is less intense compared to region II. Occurs mostly between the concentration range of 3.5-11 ppm P in solution. In some soils there is a slight tendency

Table 7. The observed C (equilibrium solution concentration of P) and x/m values (adsorbed P) at the apparent monolayer coverage of P adsorption, and the adsorption maximum calculated using the Langmuir equation

Soil	Particulars[a]			Observed		Langmuir Adsorption Maximum (ppm)
				C (ppm)	x/m (ppm)	
Wahiawa	10	144	Ca	8.0	894	738
	20	144	Ca	8.0	1003	857
	30	144	Ca	8.6	1191	999
	25	144	Ca	10.0	1030	900
	25	144	KH_2PO_4	10.5	650	666
	25	12	KH_2PO_4	12.5	550	603
Akaka	25	144	Ca	7.6	8847	8000
	25	12	KH_2PO_4	69.8	6090	5592
Naalehu	25	144	Ca	10.0	1950	1346
Hanipoe	25	144	Ca	10.5	4000	4464
Red Soil, Coimbatore	10	144	Ca	11.1	180	186
	25	144	Ca	10.8	224	254
	25	144	KH_2PO_4	11.1	116	182
Red Soil, SVRP	25	144	Ca	16.5	110	115
	25	144	KH_2PO_4	13.8	55	60
Low Level Laterite, Vallam	10	144	Ca	8.6	260	311
	25	144	Ca	10.0	345	394
	25	12	Ca	10	225	271
Low Level Laterite, Pallathur	25	144	Ca	6.2	325	416
High Level Laterite, Nanjanad	25	144	Ca	5.5	900	1056
High Level Laterite, Doddabedda	25	144	Ca	12.5	2250	2221

[a]Values given are Temperature (°C), Equilibration Time (hours) and Ionic Environment (0.01 M $CaCl_2$+$Ca(H_2PO_4)_2$ given as Ca and KH_2PO_4 in water given as KH_2PO_4) in that order.

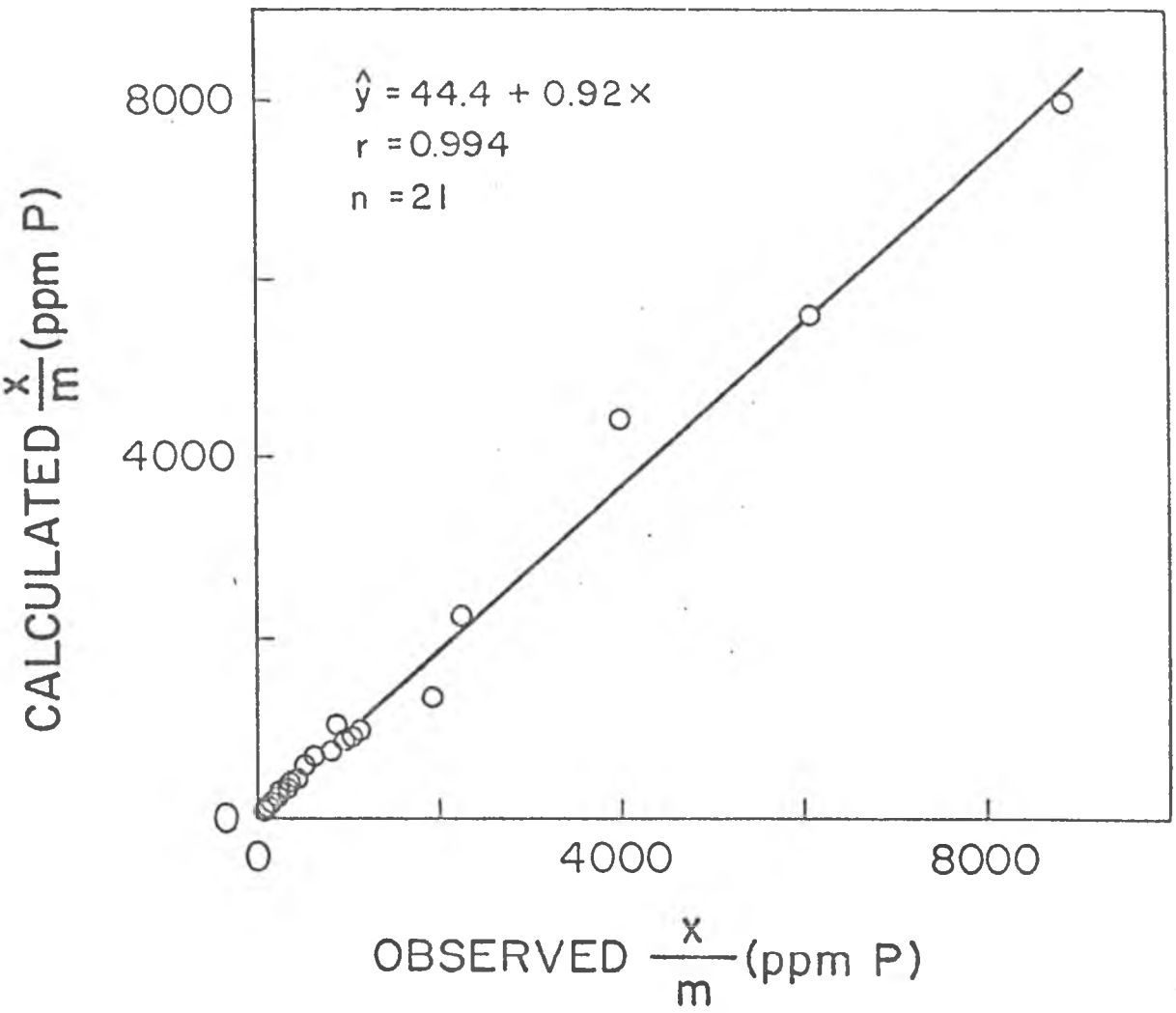


Fig. 15-Relationship between observed and calculated (Langmuir's b_{max}) P adsorption values for monolayer saturation of P reactive sites of some non-calcareous soils

towards linearity.

Muljadi, et al. (1966) studying pure soil components reported three regions related to affinity of P for three energetically different types of reaction sites. Although regions I and II described above resemble to some extent those observed by Muljadi, et al., region III does not accord with their classification. The definite linearity obtained by them was not observed here.

The three regions were examined in greater detail by plotting the isotherm data as per the equation of Shapiro and Fried (1959).

$$\text{Soil P} = -K \frac{\text{Soil P}}{P} + \text{Soil}$$

In accordance with the terminology used here the above expression can be written as

$$x/m = -K \frac{x/m}{C} + b$$

where

x/m = amount of P adsorbed µg/g soil

K = an apparent dissociation constant for the system at a specified pH

C = equilibrium solution concentration µg/ml

b = amount of P adsorbed when all the adsorption sites are saturated with P

The above equation was derived from mass action considerations, an expression formally analogous to the Langmuir equation, on the assumption that phosphate adsorption was primarily an exchange reaction with another ion such as hydroxyl. As given in the equation, a plot of x/m vs $\frac{x/m}{C}$

should yield a straight line for sites of constant adsorption energy. The data for Wahiawa soil is plotted accordingly in Figure 16. Akaka, Hanipoe and Naalehu soils are represented in Figure 17. The curves in all the plots can be separated into their linear components as indicated in the figures. In Wahiawa, Akaka and Naalehu soils only three slopes can be identified. In the Hanipoe soil, although four components are present, only three belong to the apparent monolayer region. Each slope here represents the group of sites which are energetically different from the region represented by a different slope. A comparison of slopes among different soils reveals the following inferences. The slopes of three components of Akaka soil are very similar to that of Wahiawa, and Naalehu is similar to Hanipoe. The results for the Wahiawa and Akaka soils will be discussed in conjunction with the mechanism of P adsorption by these soils later in this section. Similar behavior for Naalehu and Hanipoe is not surprising considering the similarities in their properties. Furthermore both soils originated from volcanic ash. All the curves in Figure 16 and 17 resemble the earlier reports by Shapiro and Fried (1959) and Fried and Broeshart (1967). However, the presence of definite linear components is more obvious in the present investigation.

Although the plots for only four soils are shown here, the data obtained for all the soils were given similar treatment. Whenever the number of points in the isotherm were adequate to delineate the slopes, the regions were marked, and traced to the respective solution concentrations. According to the equation the intercept should give the value of the maximum amount of P adsorbable by that site. However, in the presentation here the regions were delineated based on the values

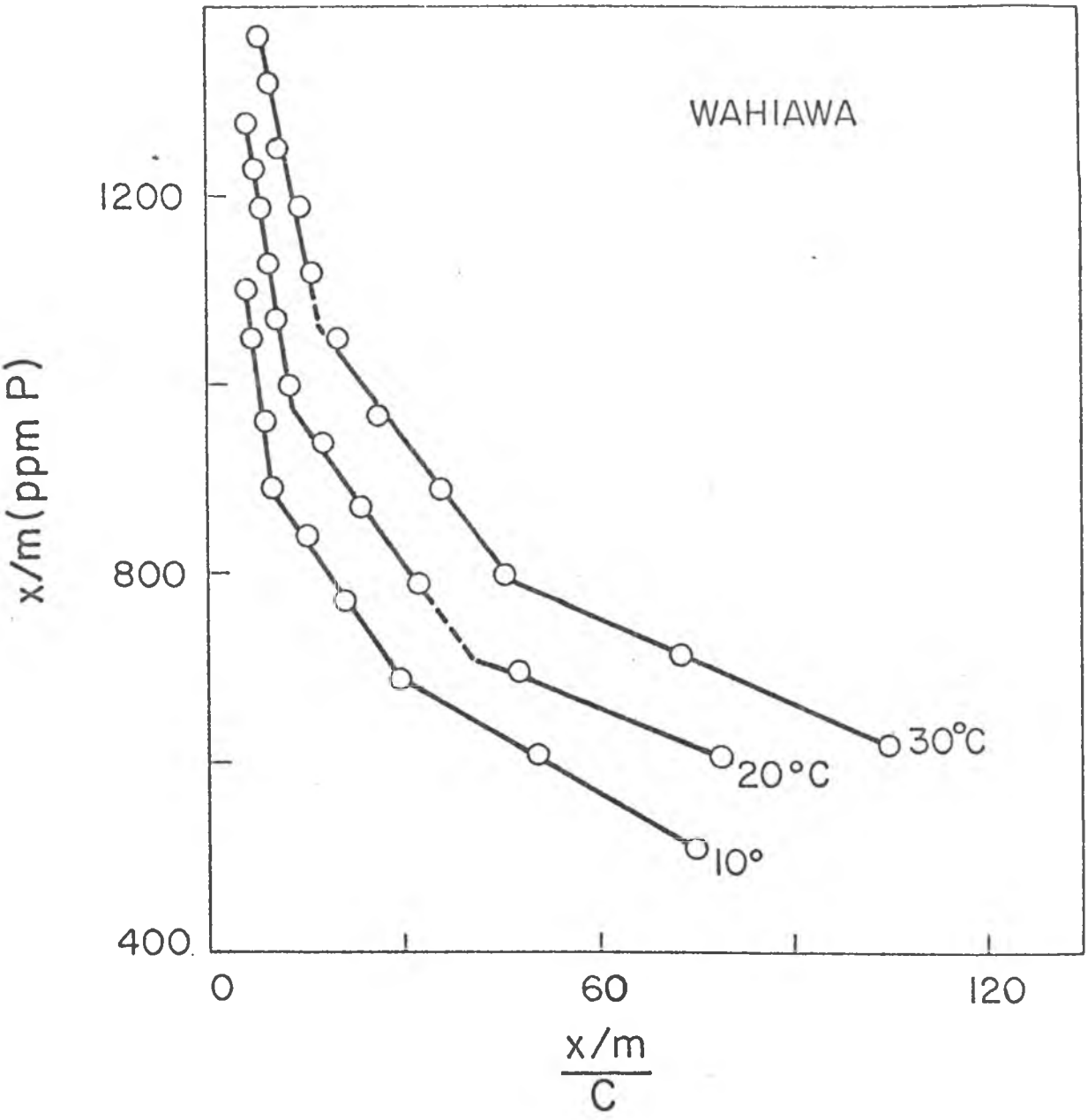


Fig. 16-P adsorption data of Wahiawa soil at three temperatures plotted according to the equation of Shapiro and Fried (1959) (C = Equilibrium solution concentration and x/m = Amount of P adsorbed)

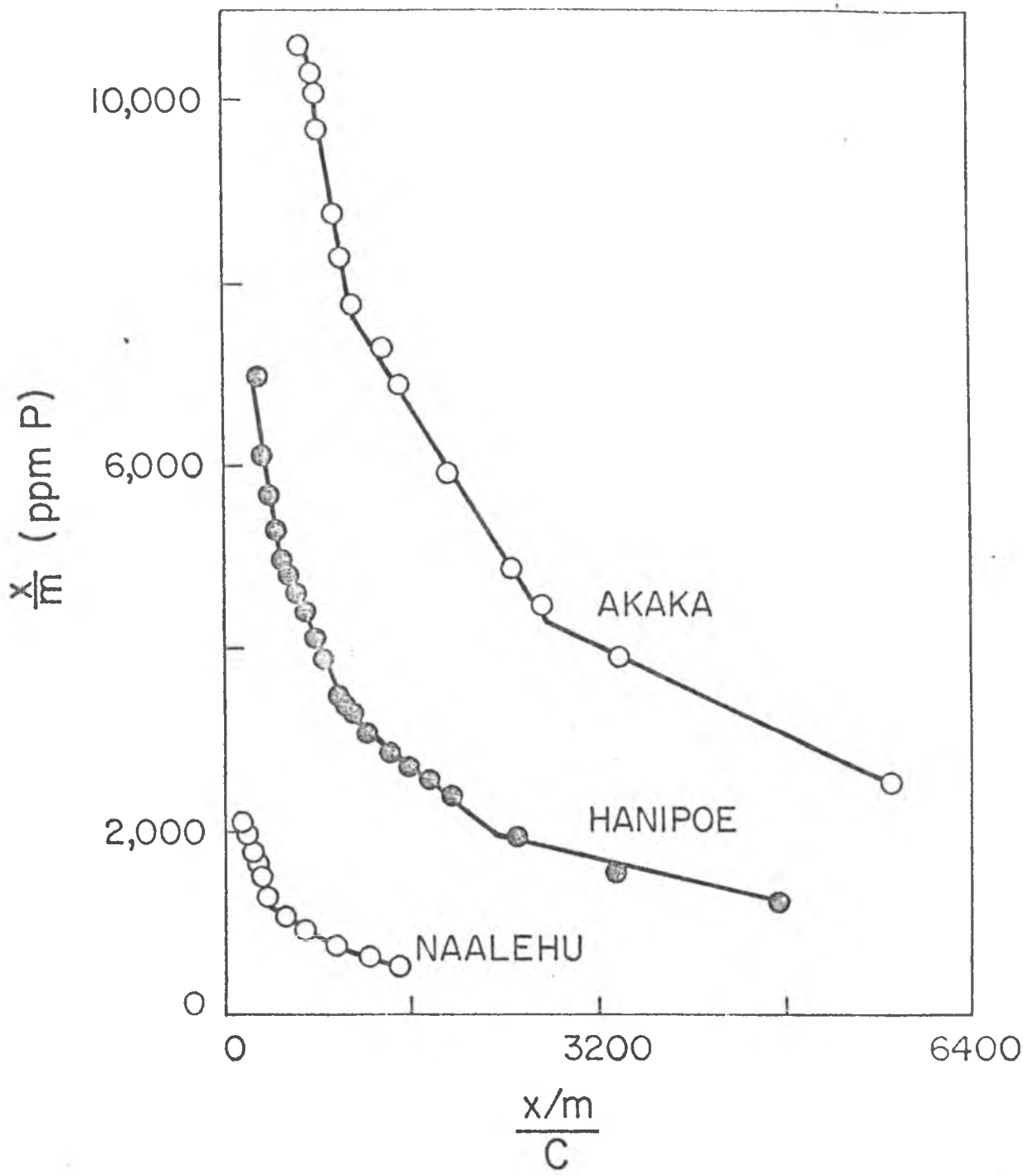


Fig. 17-P adsorption data of three Hawaiian soils plotted according to the equation of Shapiro and Fried (1959) (C = Equilibrium solution concentration and x/m = Amount of P adsorbed)

actually obtained, rather than the theoretical amount. Regions obtained in this manner correspond to the earlier description in page 63. The solution concentration (C) and x/m values at which the regions terminate are shown in Table 8. In almost all the soils regions I, II and III terminate at C values of < 1, < 3.6 and < 11 ppm P respectively. The above results seem to justify the following general conclusion: that soils of the type studied here show three definite regions of P adsorption in the apparent monolayer portion.

The treatment in terms of Shapiro and Fried's equation (1959) relates these regions to the affinity with which they are held. Significance of these regions and their importance to P availability to crops are still unanswered questions.

The phosphate sorption studies were extended to trace the shape of isotherms at higher concentrations. As was seen in Figures 9 to 14, an abrupt increase in P adsorption occurred after the apparent monolayer region. The inflection point persisted despite the change in the equilibration time (Figures 9, 14), ionic environment (Figures 9, 12, 13) and temperature (Figures 34, 35). The present result is particularly significant because a literature search did not produce another clear cut example of P adsorption after monolayer region. The logical question was: what would happen if the isotherm is continued further? To answer this question the isotherms were extended to 80 ppm P in the equilibrium solution using the two Low Level Laterites, Vallam and Pallathur, and to 45 ppm using the Red Soil, SVRP. The isotherms are illustrated in Figures 12 and 14. Since this type of P adsorption isotherms are not usually observed they are described in a detail below. Three abrupt increases in P adsorption can

Table 8. Data showing the corresponding C (equilibrium solution concentration of P) and x/m values (P adsorbed by soil) where the three linear components which correspond to three regions (p.70) in the apparent monolayer portion of the isotherm terminate

Soil	Particulars[a]			Regions					
				I		II		III	
				C (ppm)	x/m (ppm)	C (ppm)	x/m (ppm)	C (ppm)	x/m (ppm)
Molokai	10	144	Ca	0.30	70	0.92	182	5.80	381
	25	144	Ca	0.50	175	2.00	350	5.50	566
	35	144	Ca	0.30	180	2.10	450	5.40	671
Wahiawa	10	144	Ca	0.27	414	2.34	688	7.80	894
	20	144	Ca	0.40	517	1.70	736	7.60	1003
	30	144	Ca	1.00	715	2.50	894	6.80	1123
	25	144	KH_2PO_4	0.83	405	-	-	7.50	600
Kapaa	10	144	Ca	-	-	1.66	1767	5.48	2290
	25	144	Ca	1.25	2175	3.45	2750	8.10	3338
Akaka	25	144	Ca	0.21	2396	1.40	4300	7.20	7800
	25	12	Ca	-	-	42.0	5250	69.8	6090
Naalehu	25	144	Ca	0.90	860	3.20	1320	10.74	1985
Hanipoe	25	144	Ca	0.73	1980	2.50	3260	11.85	5000
Red Soil, Coimbatore	10	144	Ca	-	-	0.90	83	6.80	164
	25	144	Ca	-	-	0.67	86	8.89	222
	35	144	Ca	0.50	90	1.69	166	6.90	270

Table 8. (Continued) Data showing the corresponding C (equilibrium solution concentration of P) and x/m values (P adsorbed by soil) where the three linear components which correspond to three regions (p.) in the apparent monolayer portion of the isotherm terminate

Soil	Particulars[a]			Regions					
				I		II		III	
				C (ppm)	x/m (ppm)	C (ppm)	x/m (ppm)	C (ppm)	x/m (ppm)
Red Soil, SVRP	25	144	Ca	-	-	1.25	46	16.60	108
Low Level Laterite, Vallam	25	144	Ca	-	-	1.40	192	7.90	324
	30	144	Ca	1.04	200	10.45	341	-	-
	25	12	Ca	-	-	-	-	11.00	238
Low Level Laterite, Pallathur	25	144	Ca	-	-	3.50	230	6.8	303
High Level Laterite, Nanjanad	25	144	Ca	0.60	430	1.78	664	5.25	895
High Level Laterite, Doddabedda	10	144	Ca	-	-	1.35	990	4.70	1400
	25	144	Ca	-	-	1.50	1300	10.20	2194

[a]Values given are Temperature (°C), Equilibration Time (hours) and Ionic Environment (0.01 M $CaCl_2$+ $Ca(H_2PO_4)_2$ given as Ca and KH_2PO_4 in water given as (KH_2PO_4) in that order.

be noticed in Figure 14, at concentrations of roughly 10, 26, and 49 ppm. Even the isotherm based on data from 12 hours equilibrium shows this pattern although the magnitude is less. Since the concentration range is smaller, only two inflection points are present in Red Soil. These abrupt increases in P adsorption and the short sections of the curve following it, collectively called "humps" occur after a linear region of the curve. The position of these "humps" on two soils is summarized in the following table (Table 9).

The table shows a prolonged linear region before reaching the third "hump." The magnitude of infection III is also much greater than I and II. The present stage of knowledge does not permit an assessment on the significance of these results. A more detailed study is required to explain the specific properties related to the formation of the "humps."

More than one explanation may account for the lack of previous reports on the presence of "humps." One reason is that most work involved fewer points with wide concentration ranges. The humps may be unrecognizable in this kind of isotherm. As can be seen from the isotherm plots presented, omission of even one or two observations could lead to a smooth plot.

Before examining the processes operating at the regions of sudden increase in P adsorption, it is appropriate to consider first the mechanism of P adsorption at the apparent monolayer region. To this end an experiment was set up using Wahiawa, and Akaka soils, to study the effect of P adsorption on the desorption of OH^-, $SO_4^=$ and Si. Potassium dihydrogen phosphate dissolved in water was used as the equilibrating solution. Reaction time was 12 hours with continuous shaking. Amounts

Table 9. Extent of linear region preceding the "hump", in terms of the P solution concentration interval, and the magnitude of marked increase in P adsorption at the inflection points

Soil	Inflection Point Number	Extent of Linear Region C (ppm)	Magnitude of Rise x/m (ppm)
Low Level Laterites			
1. Vallam	I	-	57
	II	14	48
	III	21	120
2. Pallathur	I	-	86
	II	9	79
	III	22	115

of sulfate and silicon desorbed were calculated by subtracting the quantity of the anions released by the soils when water alone was used. The results are presented in Appendix Tables 4, 5 and are illustrated graphically in Figures 18 and 19. P adsorption curves for both soils exhibit definite regions of marked increase in P adsorption as concentration increased. The pH of the supernatant of both soils increased with increasing P concentrations for a time then dropped. The P solution used for equilibration decreased from 4.75 to 4.30 with increase in P. Even though both phosphate solution and soil suspension are buffered, pH increased by 0.5 units as a result of phosphate addition. In absolute terms the amount of hydroxyl released must have been much greater than was indicated by the pH shift. The pH curves closely resemble the P adsorption curves up to a 25 ppm concentration, indicating the release of OH^- groups due to phosphate adsorption.

The hydroxyl groups present in soils can also be exchanged with other anions such as sulfates and silicates. Hence, when P is added to a soil which already contains silicates and sulfates in the "exchange positions" these ions are likely to be displaced by P adsorbed. This is due to the stronger coordinate of phosphate with the metal cation than the other anions mentioned. More of silicon than sulfate was released from Wahiawa soil and more sulfate than silica from the Akaka soil. The striking resemblance of silicon and sulfate desorption curves to the P adsorption isotherm in both the soils indicate that the processes of P adsorption and the sulfate and silicon desorption are related.

The mechanism of P adsorption suggested at low P concentration in solution is presented below. Phosphate adsorption on surfaces such as

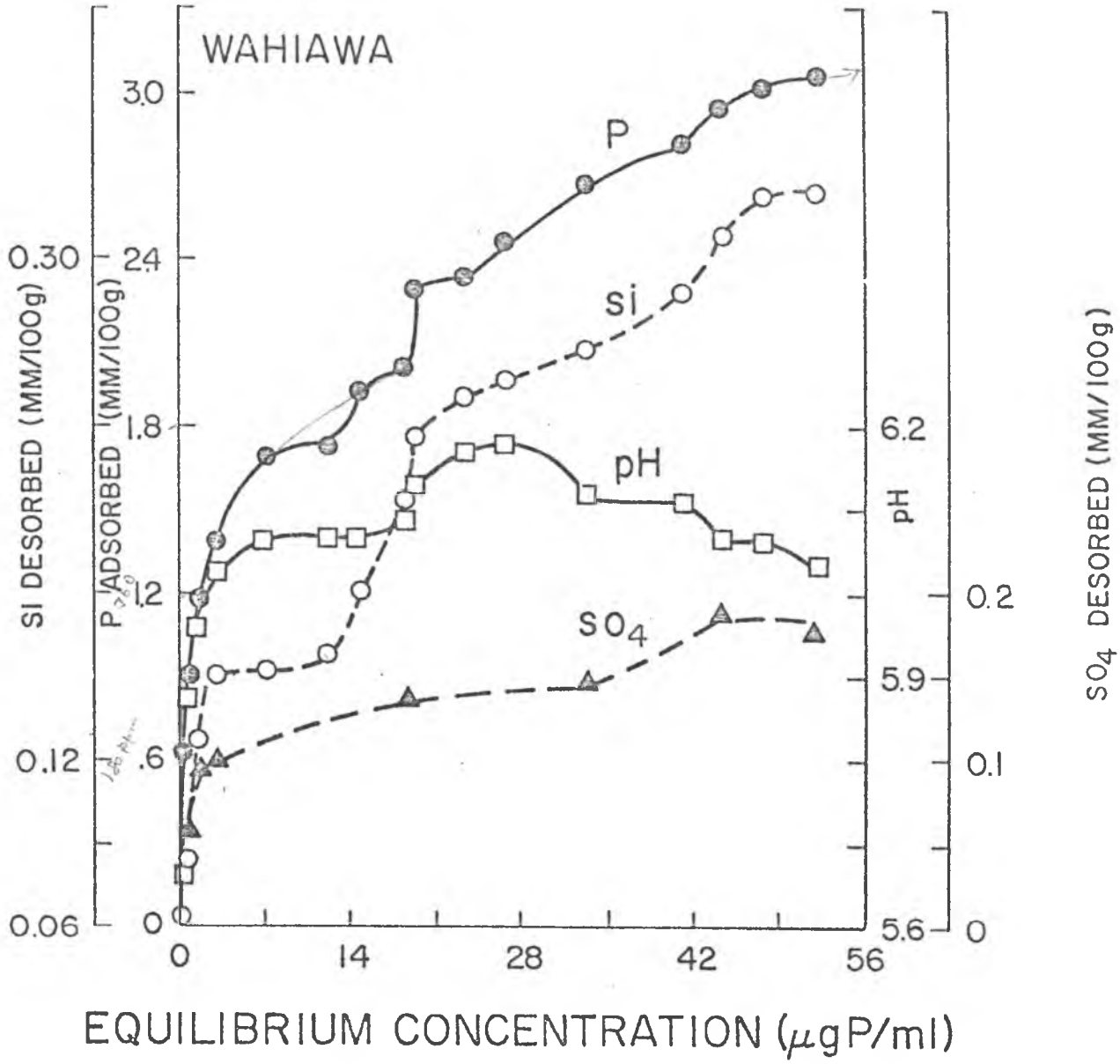


Fig. 18-P adsorption and release of Si, $SO_4^{=}$ and OH^{-} (pH) ions on addition of P to Wahiawa soil, plotted against P remaining in the equilibrium solution (12 hours equilibration, KH_2PO_4 medium)

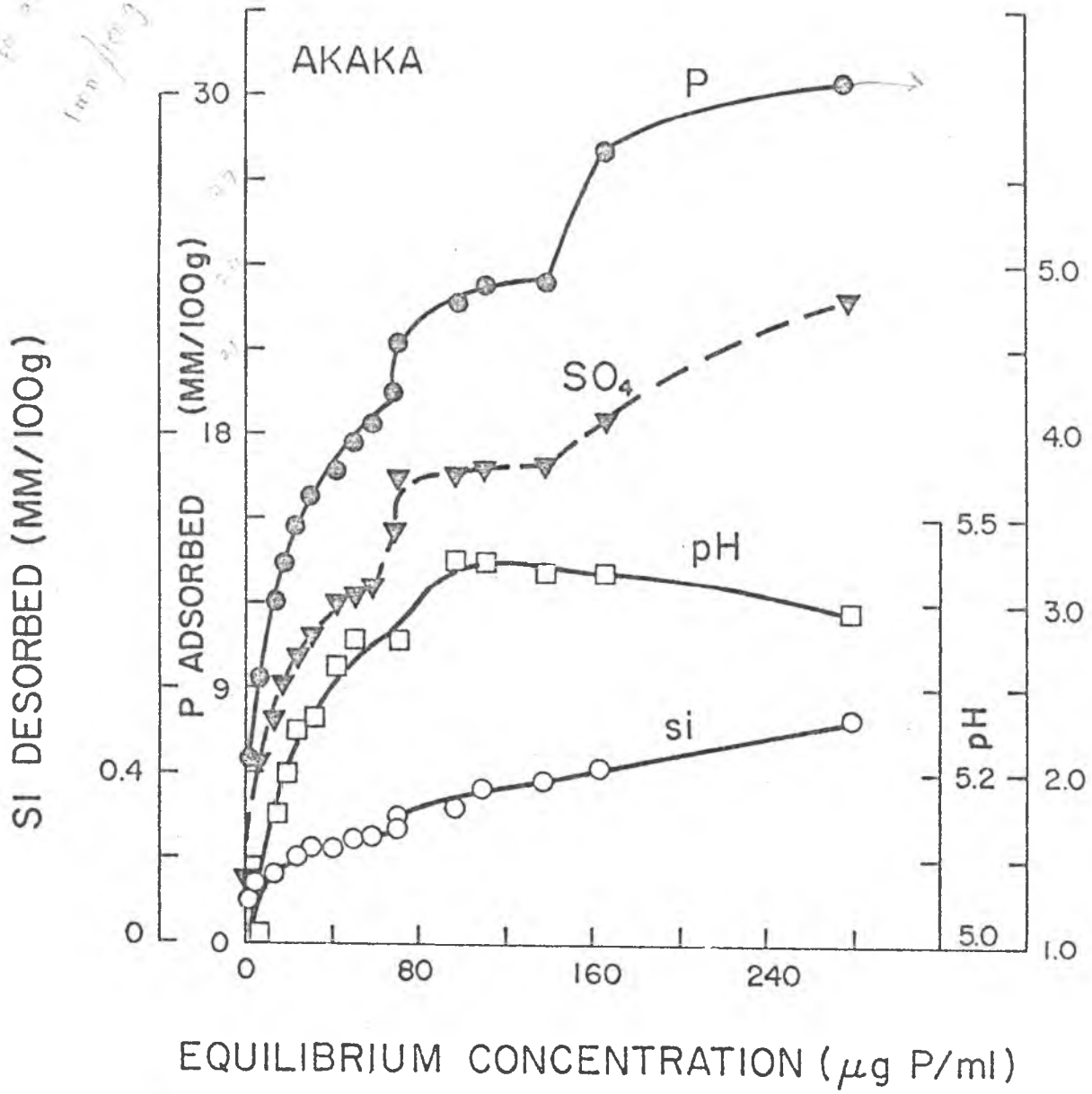


Fig. 19-P adsorption and release of Si, $SO_4^{=}$ and OH^{-} (pH) ions on addition of P to Akaka soil, plotted against the P remaining in the equilibrium solution (12 hours equilibration KH_2PO_4 medium)

those presented by gibbsite, goethite or clay edges take place by specific adsorption (Hingston, et al., 1966, 1967) which involves exchange of the anion $H_2PO_4^-$ with ligands (OH^-) coordinated to lattice metal atoms (Fe or Al). Ligands refer to the molecules or ions attached directly to a metal ion. As pointed out earlier it is iron and aluminum that are mainly responsible for P adsorption whether they are present as clay minerals or free oxides. As given in the models of Hingston, et al. (1967, 1968), increased pH, increased CEC or both are possible as a result of phosphate adsorption by ligand exchange. In Akaka and Wahiawa soils the appearance of similar slopes in relation to the energy of adsorption (p. 67) and the increase in pH evidently show that ligand exchange is happening.

Three possible explanations can be offered regarding the presence of "humps" in the P sorption isotherms at high P concentrations: (i) precipitation, (ii) presence of group of reaction sites which are energetically different, (iii) multilayer adsorption. Taking into account the short equilibration times (12 hours and 6 days) and the existing P concentration in solution, possibility of iron and aluminum phosphates precipitation is questionable. Furthermore at pHs 5 and above the activity of Fe and Al in solution is negligible. These arguments suggest that the precipitation theory is incompatible with the observations.

Soil surfaces are heterogeneous and it is probable that P reaction sites which vary energetically are present. Thus each "hump" following the primary adsorption region may represent a group of sites which are less and less reactive.

The repetitious occurrence of the "humps" with increasing solution P concentrations, gives credance to the possibility of multilayer adsorption. Two mechanisms are suggested here for additional P adsorption (Figures 20, 21). Mechanism (1) involves the exchange of hydroxyl of initially adsorbed phosphate ion with a H_2PO_4 ion, thus resulting in phosphate condensation. Since P-O-P bridge is stable (Gray and Haight, 1967), there exists the possibility of phosphate polymer formation as given in the model (Figure 20).

Phosphorus adsorption and the subsequent reactions can also create positive charges. Phosphate adsorption renders the surface negative, which results in higher cation exchange capacity of soils. Since calcium ions are available in the equilibrating solution, they should be adsorbed as exchangeable cations. Calcium adsorption may be often in excess of what is needed to neutralize the charge on the oxygen ions (Russell, 1961), which would then result in a net positive charge on the clay surface. In another part of this study the author found calcium adsorption by soils to increase with increasing P adsorption. Davis (1935) also reported adsorption of cations by Hawaiian soils at a ratio of 3 equivalents of cations (Ca and K) to one mole of P. The suggested mechanism presented in Figure 21 is based on the above considerations.

Phosphate reactions in calcareous soils. Phosphate sorption isotherms constructed for the Black soils of Coimbatore and Kovilpatty are illustrated in Figure 22. Data for the Lualualei (standard procedure) is summarized in Appendix Table 2. The isotherm for the Lualualei soil (KH_2PO_4 solutions were equilibrated for 12 hours) is plotted in Figure 23. All isotherms suggest monolayer adsorption at low

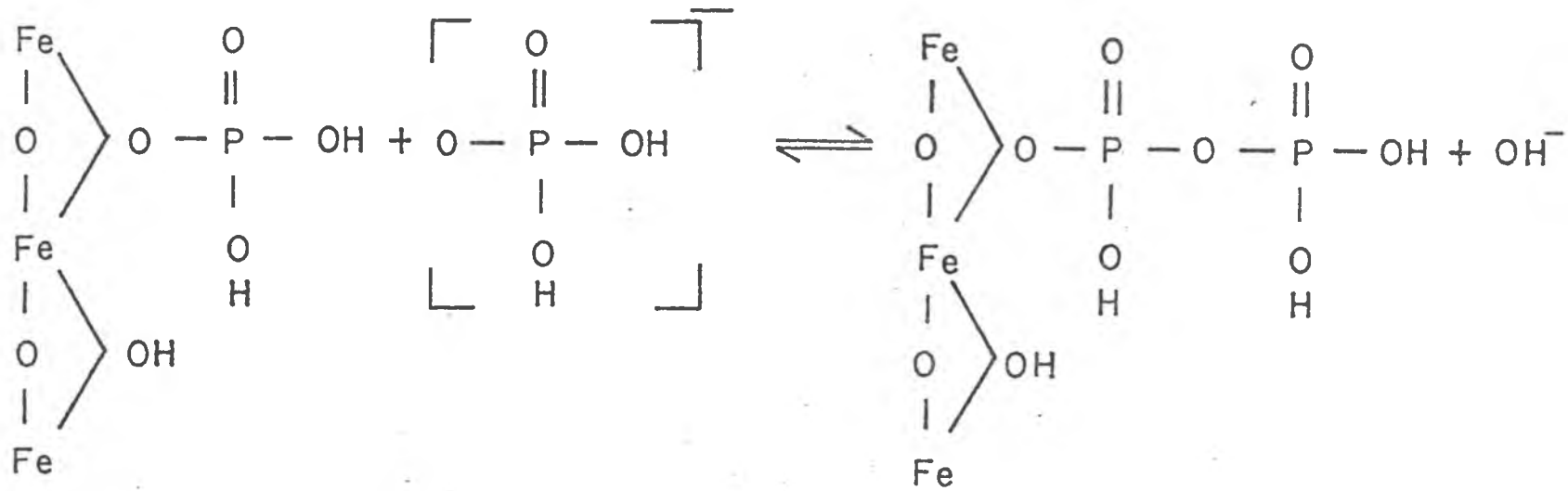


Fig. 20-Proposed mechanism of P adsorption by non-calcareous soils after saturation of primary P reactive sites (Mechanism-I; results in formation of P-O-P bridge)

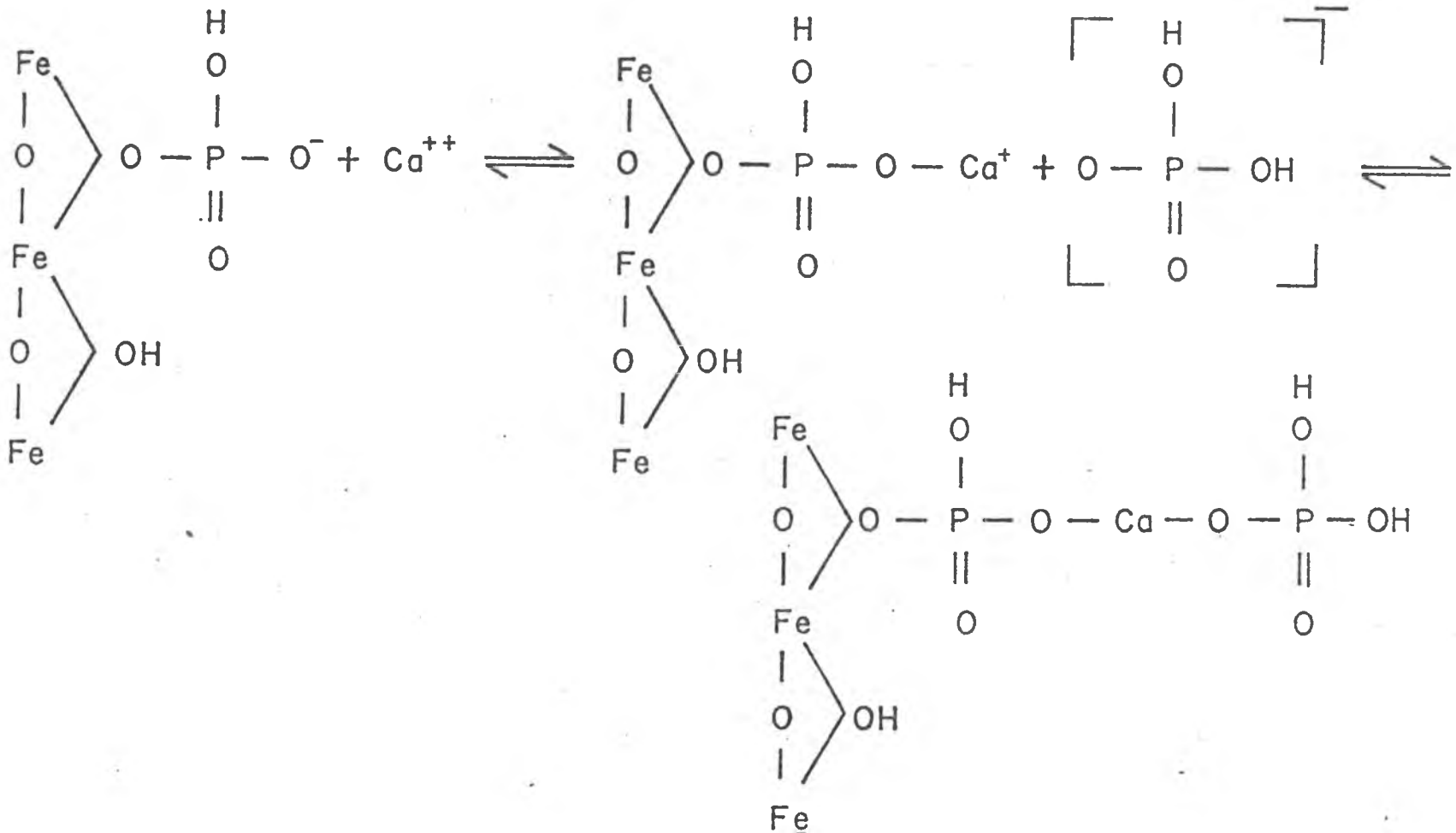


Fig. 21-Proposed mechanism of P adsorption by non-calcareous soils after saturation of primary P reactive sites (Mechanism-II; adsorption due to formation of calcium phosphate complex)

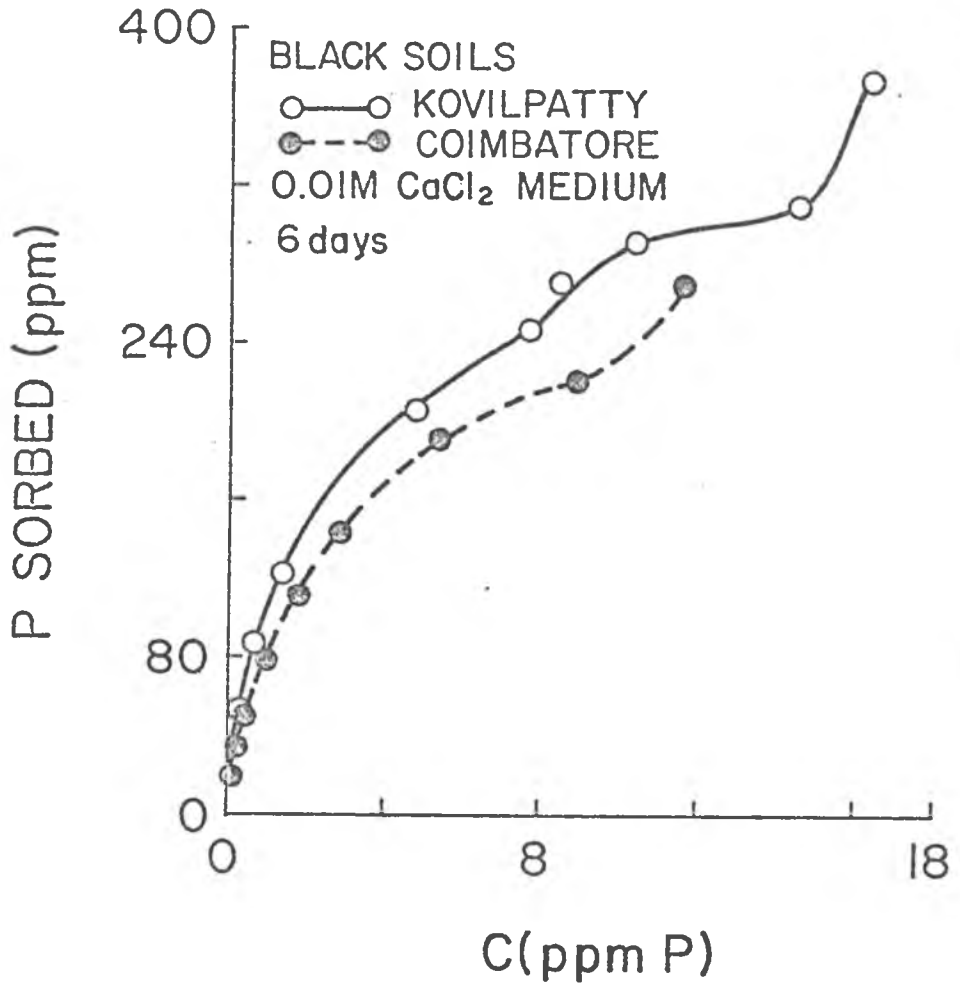


Fig. 22-Phosphate sorption isotherms of Black soils (the marked increase in P sorption occurs at roughly 9 and 16 ppm C)

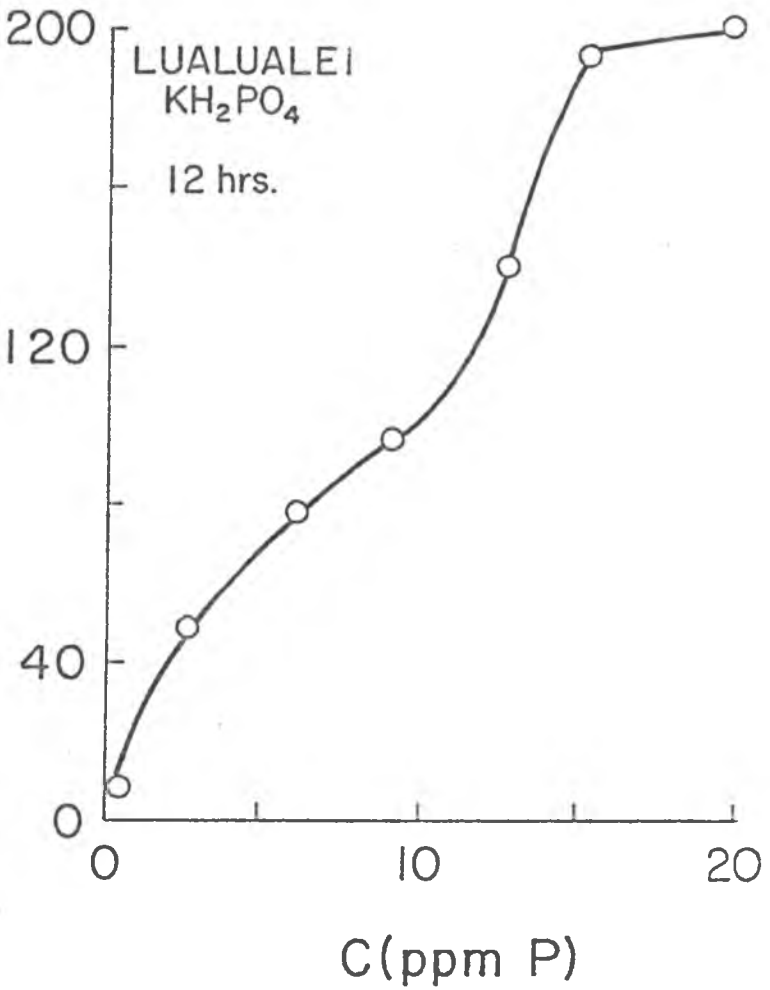


Fig. 23-Phosphate sorption isotherm of Lualualei soil

concentrations. A significant feature, however, is the marked increase in P retention after the initial monolayer adsorption region.

Phosphorus fixation in calcareous soils is largely due to (i) adsorption on $CaCO_3$ surfaces, (ii) complex formation with the Ca^{++} present in the cation exchange position of clays, (iii) precipitation as calcium phosphates and to a smaller extent due to adsorption by iron and aluminum compounds present in the clay minerals, and as impurities. These reactions can occur simultaneously and the dominant reaction (s) may vary with changing concentration. Since calcium carbonate is mainly responsible for P retention in soils which are naturally calcareous some researchers have used pure $CaCO_3$ in an attempt to understand the reactions in these soils. Thus Boishot, et al. (1960) determined the P sorption isotherms for $CaCO_3$. The isotherms obtained here closely resemble the earlier isotherms of these authors.

The portion of the isotherm preceding the inflection point probably represents P adsorption either on free $CaCO_3$ or due to the exchangeable calcium. The results of Cole, et al. (1953) and Cole and Watanabe (1957) suggested monolayer adsorption at low concentrations for reasons that, essentially all the P fixed at these concentrations were exchangeable with P^{32}, and the isotherm could be described using the Langmuir equation. Arambarri and De (1967) also reported similar results. In the present investigation the P sorption isotherms followed the Langmuir equation at low concentrations (up to 8 ppm). Cole and Olsen (1959) found that in calcareous soils P solubility is directly related to surface area and percent saturation of these surfaces with phosphate. Again this suggests that the mode of P retention at low concentration is

adsorption. A fairly close agreement existing between the calculated and observed x/m values for saturation of primary P adsorption sites indicate that adsorption is the dominant reaction occurring at concentrations lower than 10 ppm (Table 10).

The effect of P sorption on the release of hydroxyl, sulfate and silicon were investigated with Lualualei soil. The results are presented in Figure 24 and Appendix Table 6. In sharp contrast to the Wahiawa and Akaka Soils, Lualualei released only silicon and not OH^- and SO_4^- ions. This is understandable since these soils are alkaline and have no sorbed sulfate. The silicon "desorption" curve closely followed the P sorption isotherm at all P concentrations suggests that silicon release was tied to P adsorption. The amount of silicon released accounted for about 25 % of the P adsorbed. This silicon may have been released from the dark magnesium clay minerals or from "gel" material. Olsen, et al. proposed exchange of sulfates and carbonates for phosphate ions in calcareous soils. The sulfate curve of Figure 24 does not indicate this anion as being very important in alkaline soils but the possibility of CO_3 exchange cannot be ruled out.

Although P precipitation reactions accurring at high P concentrations have been confirmed, the exact nature of the precipitates is less clearly understood. Results obtained with superstition sand samples from California have important implications in fertilization of calcareous soil. The isotherms (Fig. 25) are for soil samples which had been previously treated with 0, 50, 100, 200, 400, 800, 1600 and 3200 ppm P as super phosphate. Phosphate sorption increased with increasing prior P treatments up to 800 ppm, after which the trend was reversed.

Table 10. Calculated x/m (Langmuir's b_{max}) and observed C^a and x/m^b values for monolayer adsorption of phosphorus

Soil	T°C	Calculated x/m (ppm)	Observed	
			C(ppm)	x/m(ppm)
Black Soil, Coimbatore	10	263	9.8	216
	25	251	7.7	252
	Room T	265	7.8	256
	Room T	189	8.0	208

[a] C = equilibrium solution P concentration

[b] x/m = amount of P adsorbed

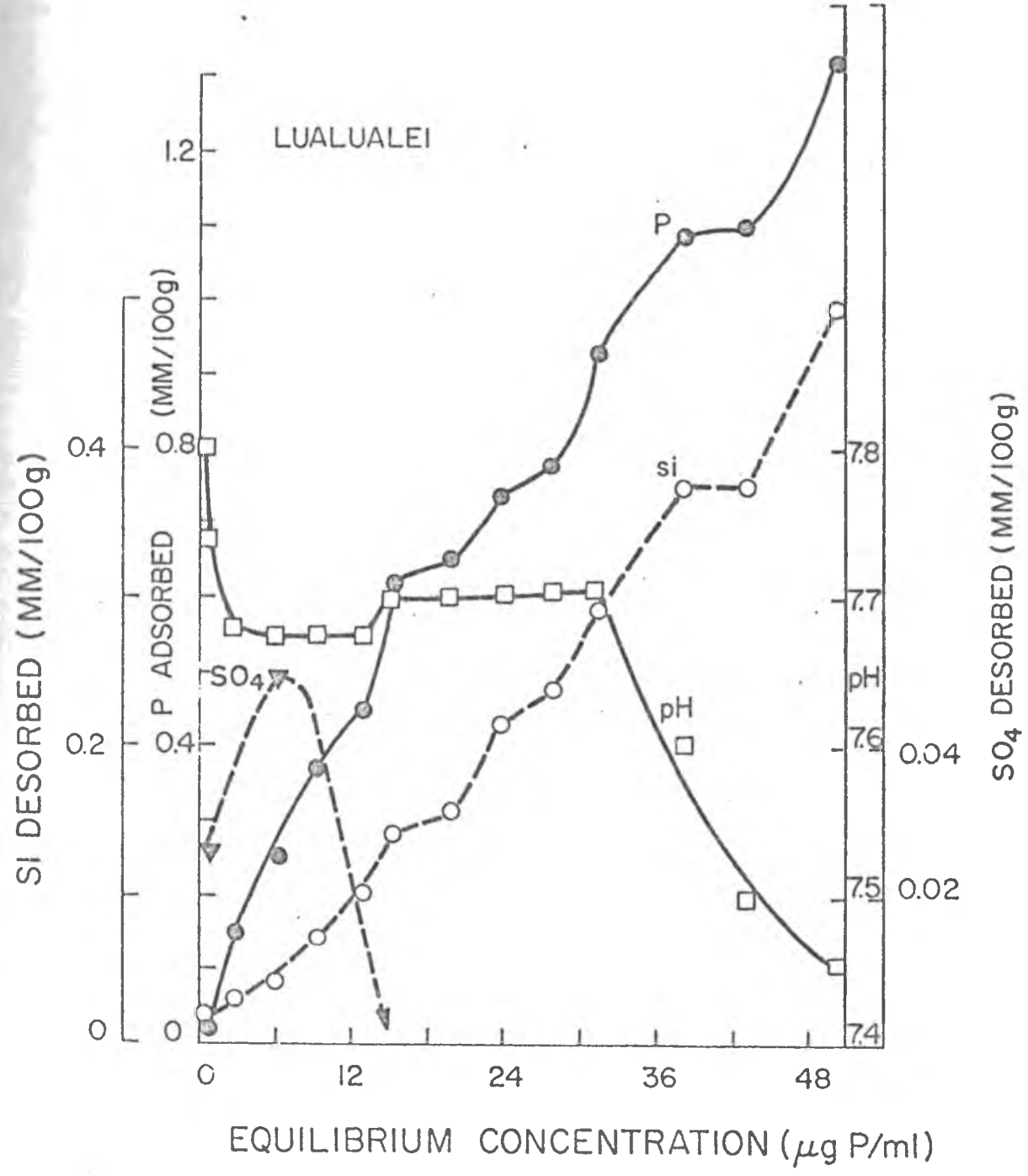


Fig. 24-P adsorption and release of Si, $SO_4^=$ and OH^- (pH) ions on addition of P to Lualualei soil, plotted against P remaining in the equilibrium solution (12 hours equilibration, KH_2PO_4 medium)

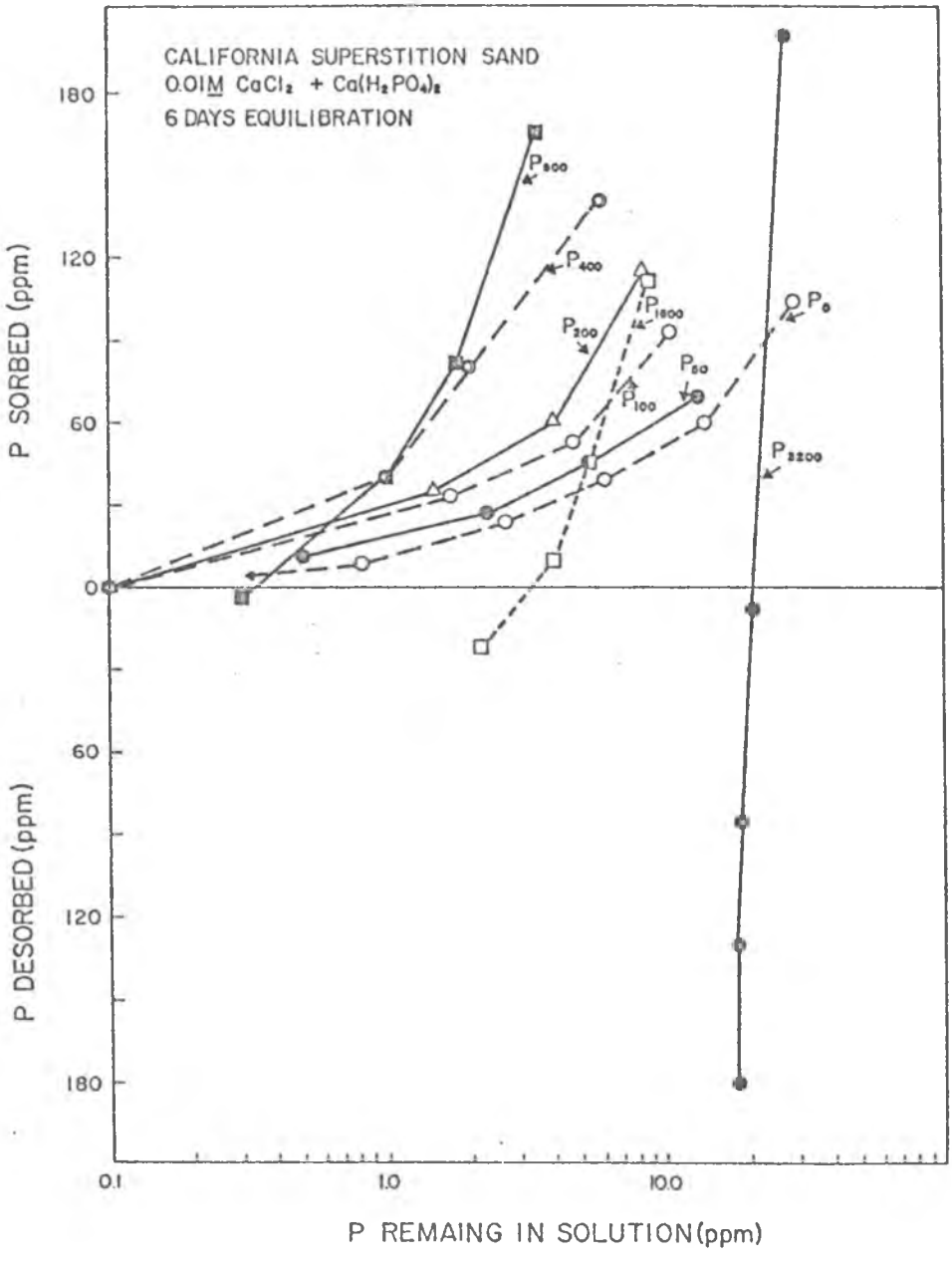


Fig. 25-Influence of prior P application on P sorption by a Superstition sand, California

Interestingly all points on the isotherm were in the range of 18 to 28 ppm P for the soil sample which originally received 3200 ppm P. Within this range till the process was desorption (points corresponding to -x/m in Fig. 25), the concentration of P in solution was maintained at 18 ppm. This concentration approximates the solubility of dicalcium phosphate dihydrate calculated by Aslyng (1954). Increasing P sorption with increasing P added initially up to 800 ppm P indicates that in calcareous soils P reactions proceed beyond adsorption even with low P applications provided the duration of equilibration is long enough.

Figure 26 demonstrates that the Langmuir's plot of the P_0 (initial) sample yields a straight line up to 14 ppm P in equilibrium solution. The calculated P adsorption maximum was 102 ppm. In other words, theoretical P requirement for monolayer adsorption by the P reactive surface is 102 ppm P. Beyond this precipitate may form. But the data presented in Figure 25 suggest that even at lower concentrations P did not remain sorbed but probably served as nuclei to precipitate P added later. Cole, et al. (1953) reported that the P adsorbed as a monolayer on $CaCO_3$ exchanged with P^{32} less readily when the reaction time was lengthened. A corollary is that, short term P equilibration studies may lead to an inaccurate evaluation of the P reactions that occur in the field, even during one crop season. However, P sorption isotherms constructed after different intervals of equilibration will be very useful in predicting the course of reaction in the field.

Numerous investigators believe that $CaHPO_4$ or a compound of similar composition is the initial precipitate formed when monocalcium phosphate is added to calcareous soils (Gardner and Kelley, 1940; Brown and Lehr,

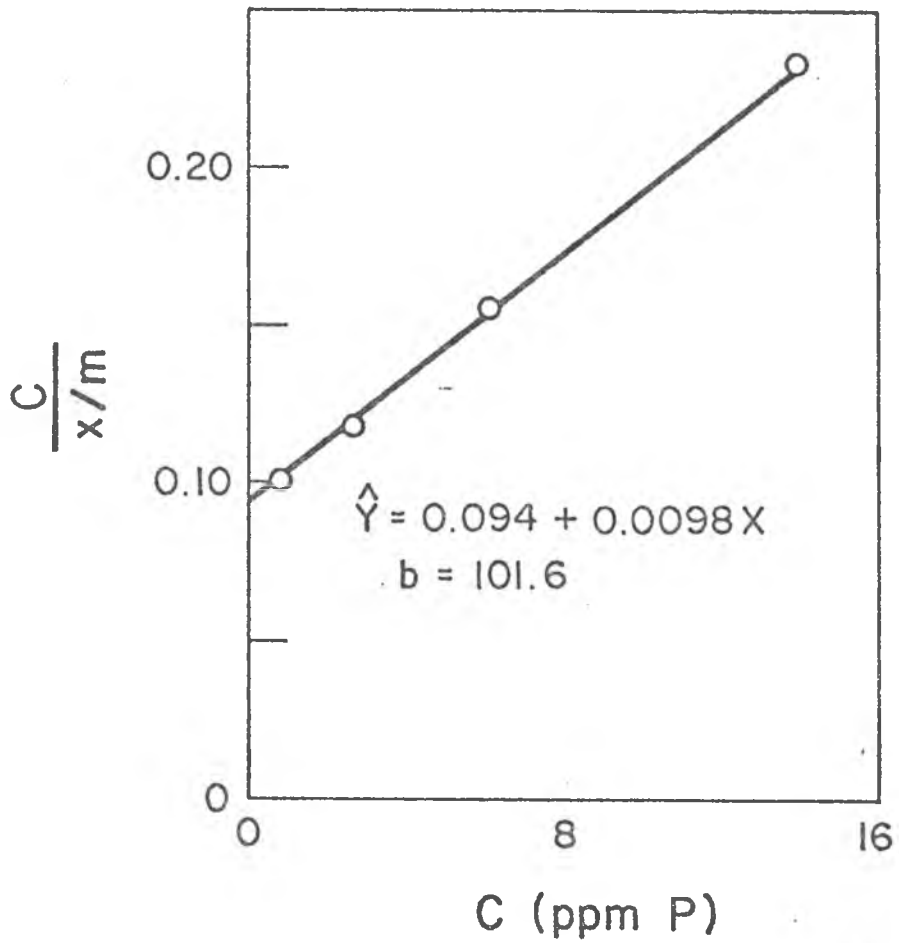


Fig. 26-The Langmuir plot of P adsorption data of the Superstition sand (P_0 sample: 6 days equilibration in 0.01 M $CaCl_2$ + $Ca(H_2PO_4)_2$ medium. b = calculated adsorption maximum)

1959; Lindsay and Stephenson, 1959). Although dicalcium phosphate is not thermodynamically stable in the presence of excess $CaCO_3$, its transition to hydroxy apatites requires prolonged periods. In nature, 18 months or longer may be required for conversion of dicalcium phosphate to less soluble forms (Cole, et al., 1953). In the sample studied here P probably exists mostly as dicalcium phosphate with a little apatite. Results indicating increased P sorption with increasing prior rate of P application is in accord with a report of Brown and Lehr (1959). They believed that partial precipitation of dicalcium phosphate through direct reaction with soil-derived calcium entails precipitation of additional phosphate.

The isotherm for the Superstition sand, to which 3200 ppm P had previously been added, was almost a vertical straight line. This suggests the formation and dissolution of mainly dicalcium-phosphate as new phosphate is added. The rate of dissolution of dicalcium phosphate is proportional to the surface area and the rate of formation is proportional to the activity of reactants in addition to surface area. The rate of surface crystal growth is equal to the rate of dissolution when the solution is saturated with P (Marshall and Nancollas, 1969). It is possible that the solution of the sandy soil used here was saturated with P when the P application reached a level as high as 3200 ppm. The P concentration in solution maintained here was between 21 to 28 ppm P when there was no net loss of P by soil. This approximates the solubility of $CaHPO_4.2H_2O$ in 0.01 M $CaCl_2$ at pH 6.11 (29 ppm) calculated by Olsen, et al. (1960).

Fitting P adsorption data to theoretical models. Calibration of adsorption data using theoretical models is desirable, as it may aid in measuring the size of the P adsorption system. The Langmuir and the Freundlich equations have been widely used for describing P adsorption by soils. While the Freundlich equation is an empirical one, the Langmuir equation invokes the theory of limiting adsorption to a monolayer. Although all the adsorption data obtained in this study (except Lualualei at equilibration time of 12 hours in KH_2PO_4) fit the Langmuir equation, four Hawaiian soils are plotted in Figure 27. These show a high degree of variation in adsorption maxima. Figure 28 illustrates the adsorption data for Low Level Laterites of India.

According to Langmuir equation a plot of $\frac{C}{x/m}$ against C yields a straight line and the reciprocal of the slope gives the adsorption maximum. Pertinent information regarding adsorption maxima of different soils and the concentration range up to which the data follow the Langmuir equation are given in Table 11. Although the straight line fits only to a shorter concentration range for the data obtained by the standard procedure, 12 hours equilibration of soil with KH_2PO_4 gave a good fit up to 12 ppm P in solution for the Wahiawa soil and 42 ppm for the Akaka soil.

The Langmuir isotherm was found to give a good fit for describing P desorption data also (Figures 29, 30). This is helpful in that using two constants of the equation (a and b), it should be possible to predict equilibrium solution concentration of P at very high dilutions. However, values for the adsorption maxima for the Wahiawa and Akaka soils are unrealistic. Despite some of the assumptions (Adamson, 1960) involved

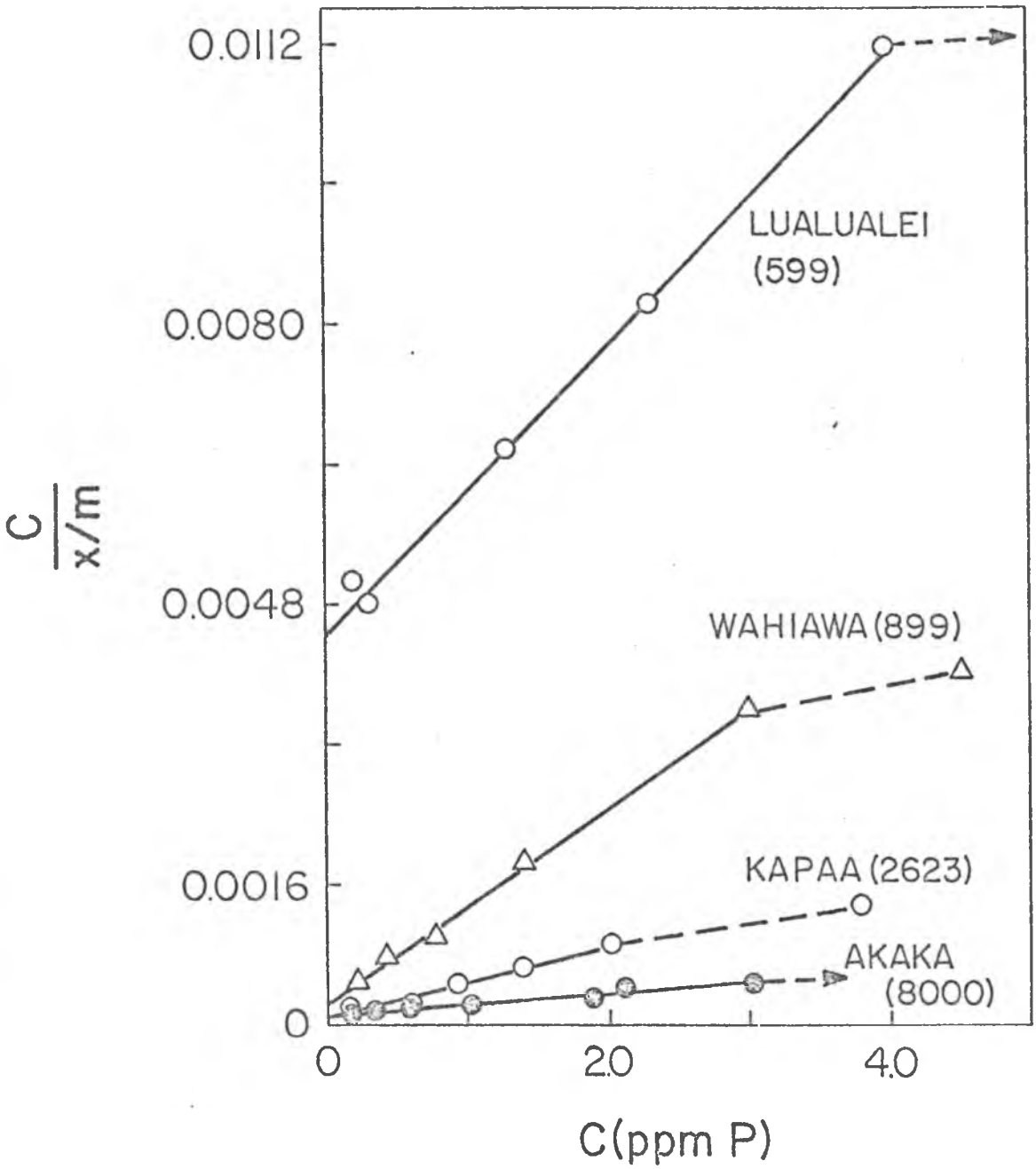


Fig. 27-Linear plots of the Langmuir isotherm of contrasting Hawaiian soils. Values in parentheses are calculated P adsorption maxima (8 and 6 days equilibration for Lualualei and other soils. $CaCl_2$ medium)

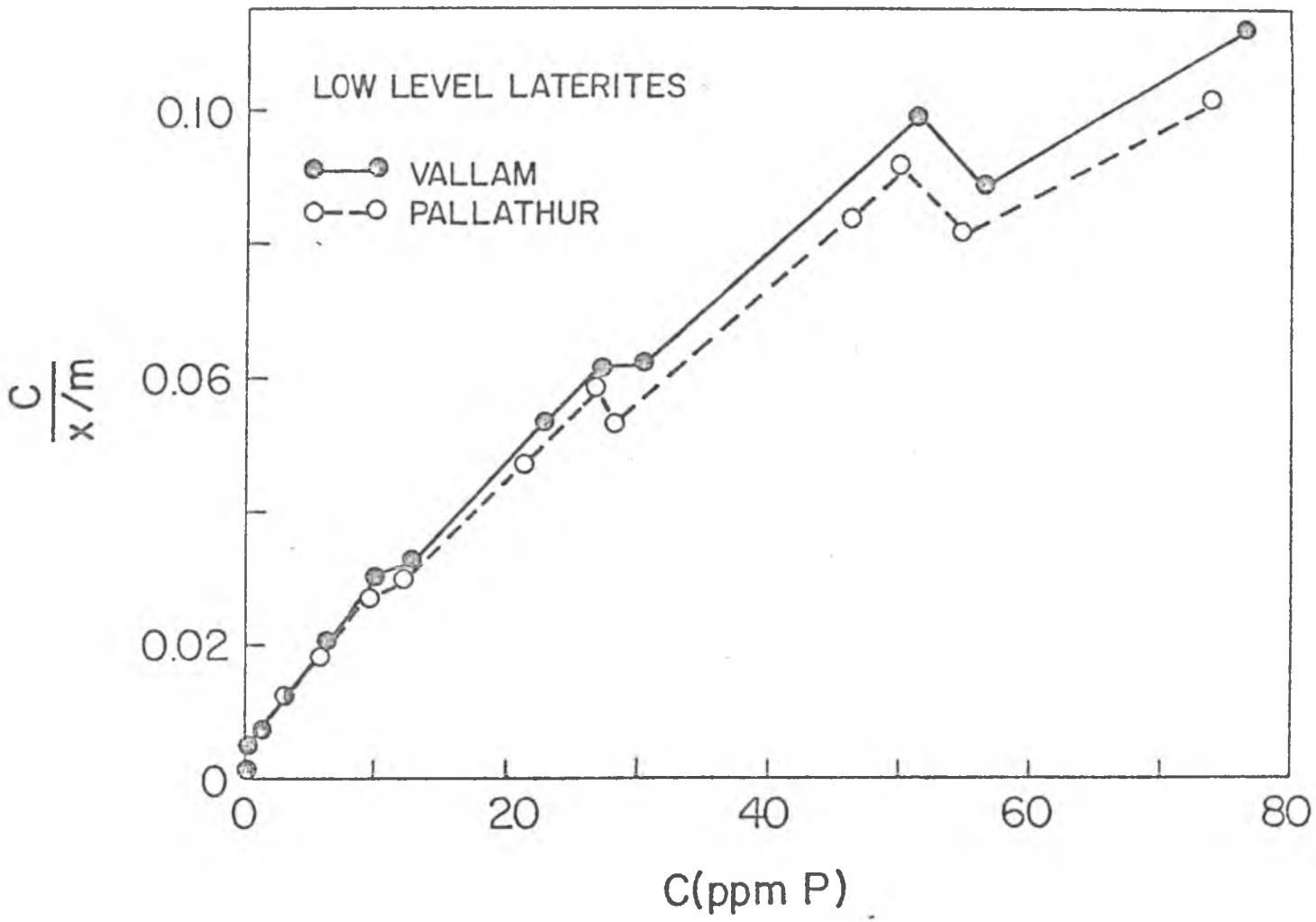


Fig. 28-The Langmuir plots of P adsorption isotherms of Low Level Laterites
(Each straight line corresponds to a "hump")

Table 11. Phosphorus adsorption maxima (b_{max}), the concentrations (C) up to which the best fit for the Langmuir equation was obtained and the number of observations (n) used in the straight line fit. All r values exceeded 0.996 except for the Wahiawa soil.

Soil	Desorption Data b_{max} (µg/g)	C (µg/ml)	n
Adsorption Data			
Hawaiian Soils[a]			
Lualualei	599	4.04	5
Molokai	566	3.43	5
Wahiawa	899	1.99	5
Kapaa	2623	2.37	5
Naalehu	1346	2.02	6
Maile	10506	4.84	8
Hanipoe	4464	3.57	10
Akaka	8000	3.21	7
Indian Soils[a]			
Black Soil, Coimbatore	287	8.99	6
Black Soil, Kovilpatty	189	2.57	5
Red Soil, Coimbatore	254	8.89	5
Red Soil, SVRP	115	11.36	4
Low Level Laterite, Pallathur	416	9.60	4
Low Level Laterite, Vallam	394	10.32	4
High Level Laterite, Nanajanad	1056	5.25	6
High Level Laterite, Doddabedda	2221	5.30	6
Hawaiian Soils[b]			
Lualualei	No straight line fit		
Wahiawa	603	12.51	5
Akaka	5592	41.83	7
Desorption Data[c]			
Lualualei	455	4.06	8
Molokai	588	4.67	9
Wahiawa	11111	4.59	8
Akaka	102041	6.04	10

[a]6 days equilibration in 0.01 M $CaCl_2$ + $Ca(H_2PO_4)_2$ medium
[b]12 hours equilibration in KH_2PO_4 medium
[c]Extractant 0.01 M $CaCl_2$. Equilibration time 4 hours

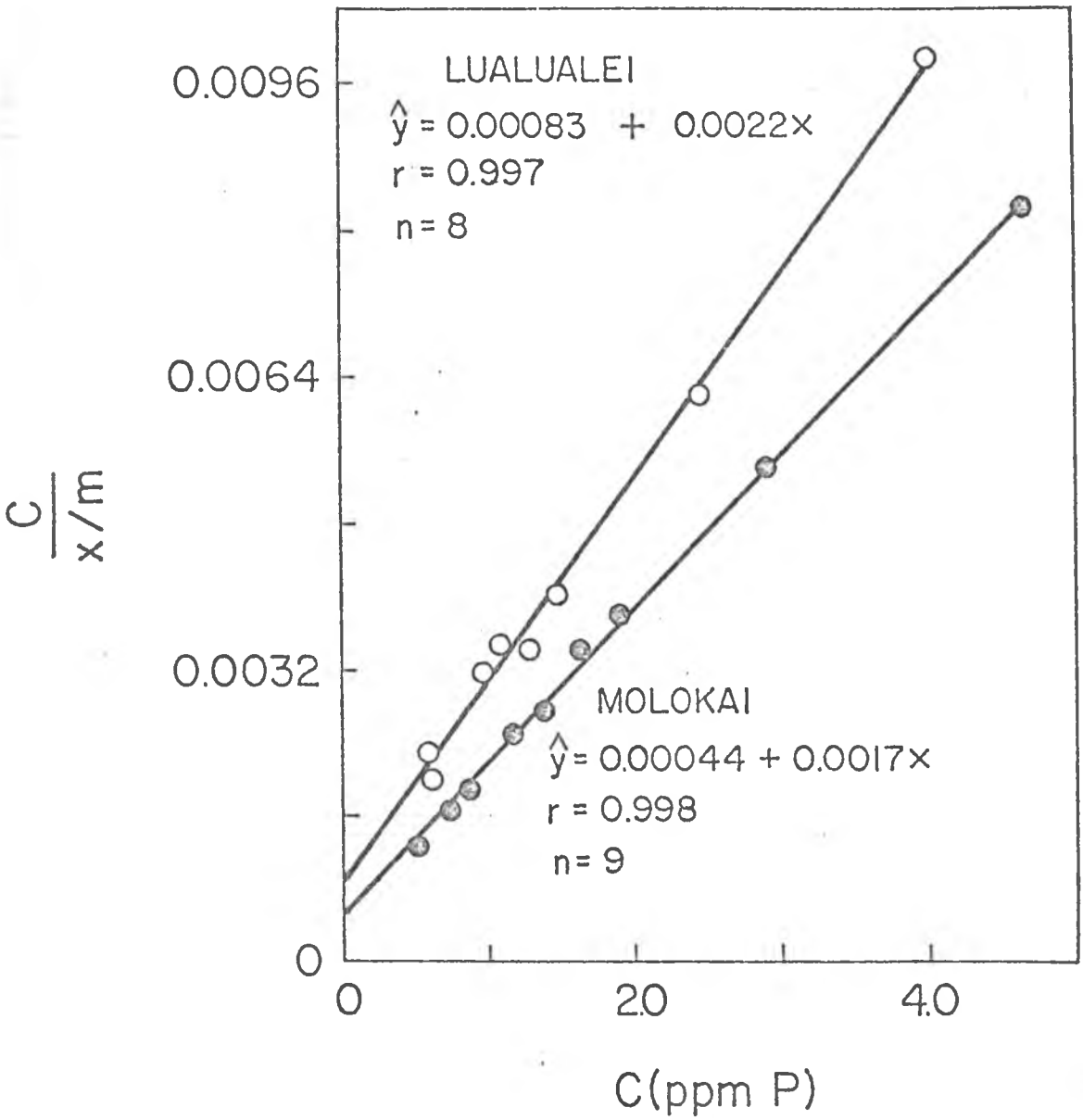


Fig. 29-P desorption data for the Lualualei and Molokai soils plotted according to the Langmuir equation (4 hours equilibration for desorption using 0.01 M $CaCl_2$)

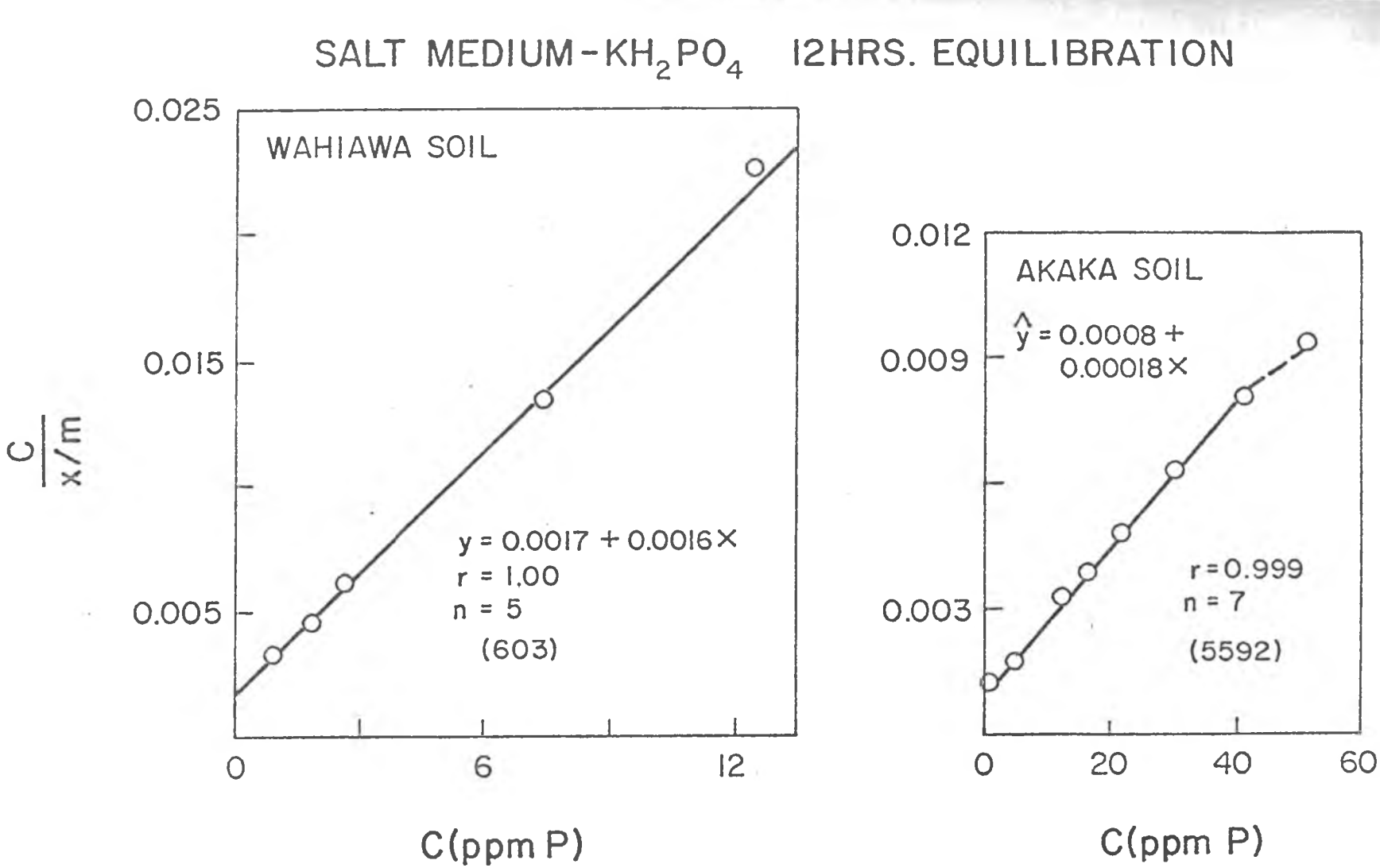


Fig. 30-The Langmuir plots of P desorption data of Wahiawa and Akaka soils. (Equilibration 4 hours. Extractant - 0.01 M $CaCl_2$)

in using the Langmuir equation, which may not really apply for a soil-P solution system, the equation is still useful for finding b_{max} and calculating the degree of P saturation of the adsorption maximum, which can be related to P uptake (Woodruff and Kamprath, 1966; Fox, et al., 1968).

Effect of temperature on P adsorption and calculation of isosteric heat of P adsorption ($\Delta\bar{H}_{x/m}$). A temperature study was undertaken to obtain data on the energy requirements of P adsorption by soils at different surface coverage of P reactive sites. Initially three temperatures were employed for the Wahiawa, Molokai and Red Soil, Coimbatore. Since a plot of Log. C, for a particular surface coverage, against 1/T yielded a straight line (Figures 31, 32), the correlation coefficient being $\geqslant 0.99$, in the subsequent samples the isotherms were constructed for only two temperatures. A simple plot of the isotherm data with x/m against C are illustrated in Figures 33 to 36. In all the soils an increase in T has resulted in higher P adsorption, thus showing that the heats of adsorption are positive. Similar results were reported by Low and Black (1950), Shapiro and Fried (1959) and Muljadi, et al. (1966).

Much of the energy absorbed by the system may have been expended in the removal of mainly hydroxyl and to a certain extent sulfate and silicate ions. The spontaneity of the reaction occurring in spite of its endothermic nature, may be due to the possible positive entropy change.

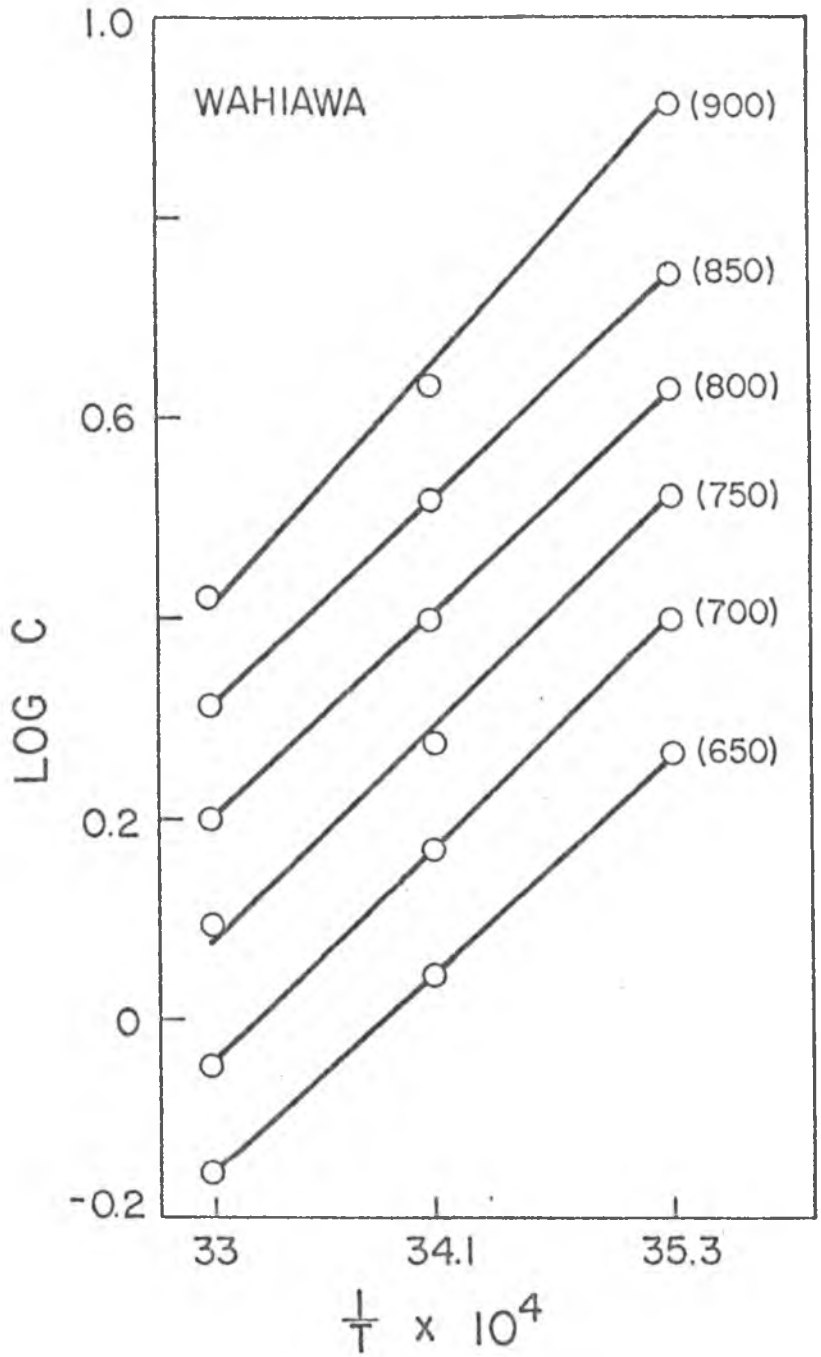


Fig. 31-Log of equilibrium solution concentration of P (C) against 1/T at various amounts of P adsorption (x/m) for Wahiawa soil (Values in parentheses are x/m)

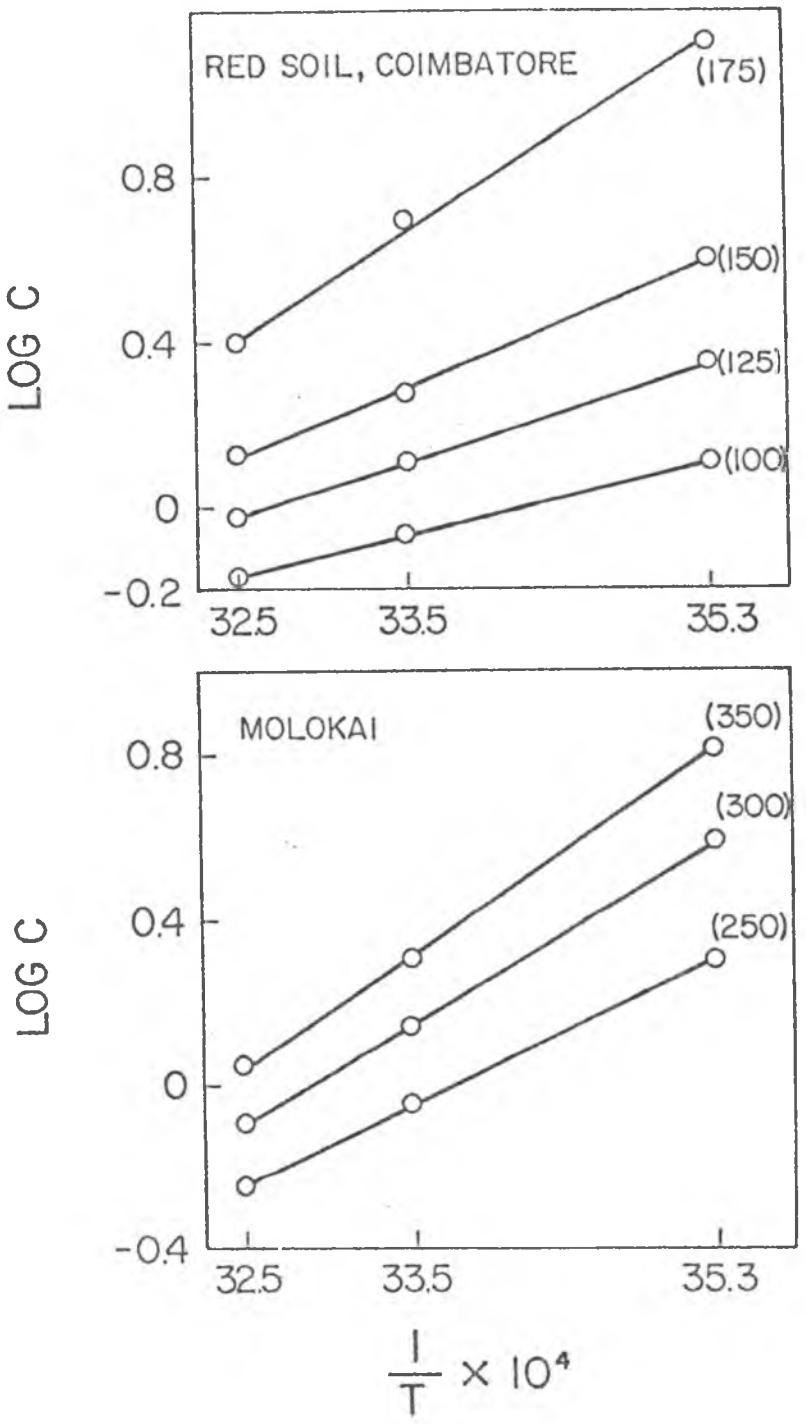


Fig. 32-Log of equilibrium solution concentration of P (C) against 1/T at various amounts of P adsorption (x/m) for Red soil, Coimbatore and Molokai soil.
(Values in parentheses are x/m)

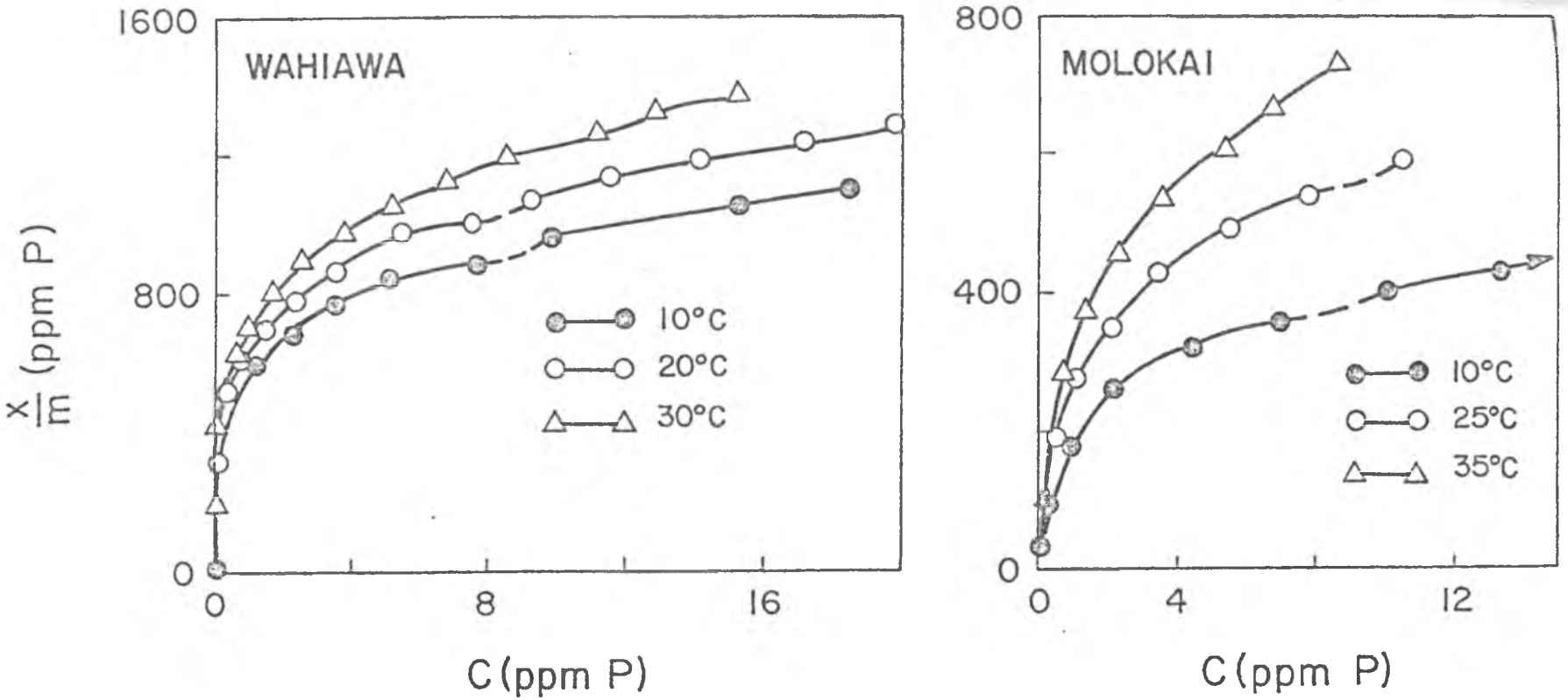


Fig. 33-Effect of temperature on P adsorption by Wahiawa and Molokai soils (C = Equilibrium solution concentration of P, x/m = P adsorbed by soil, 6 days equilibration in $CaCl_2$ medium)

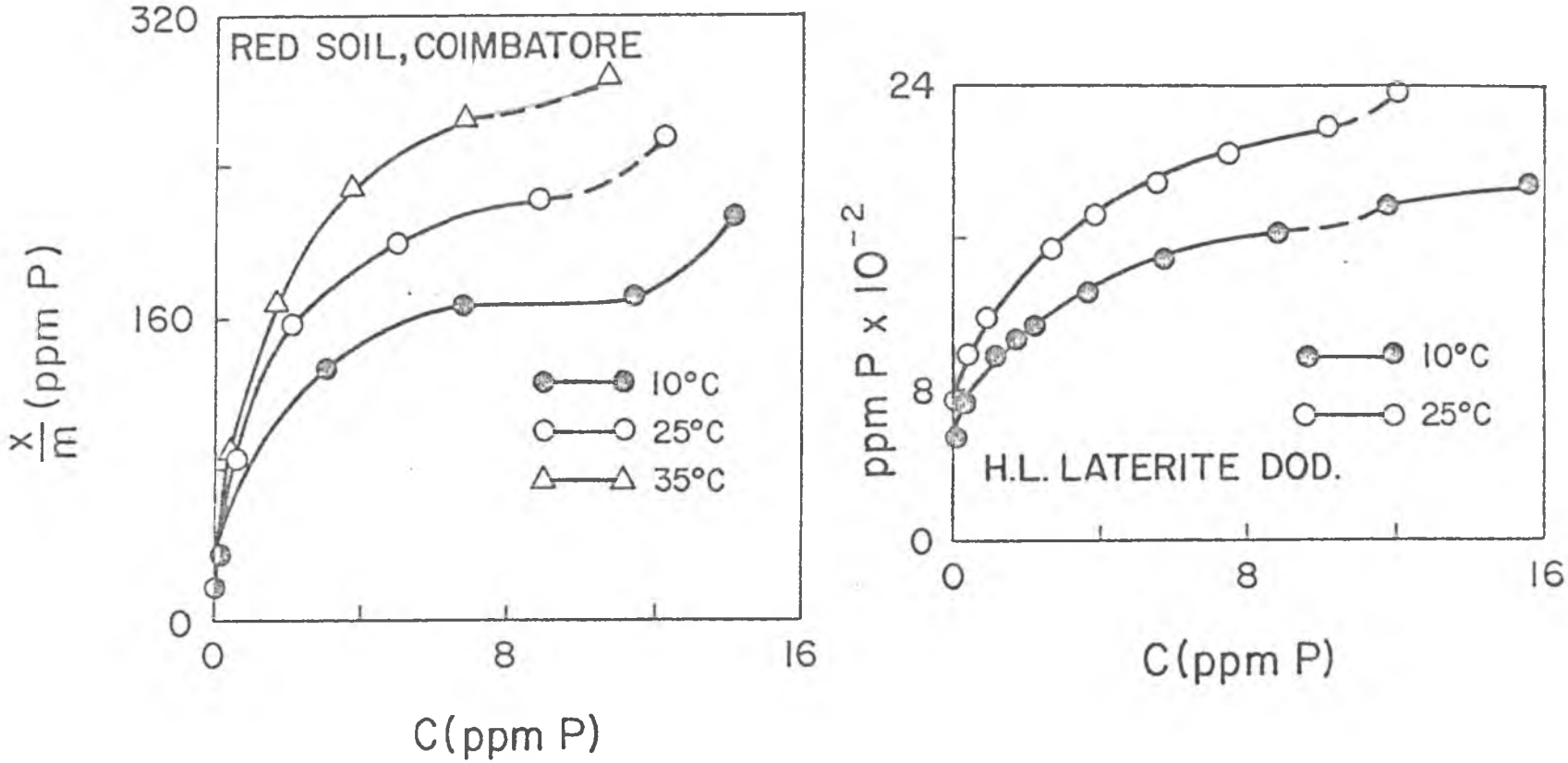


Fig. 34-Effect of temperature on P adsorption by Red soil and a High Level Laterite (6 days equilibration in $CaCl_2$ medium)

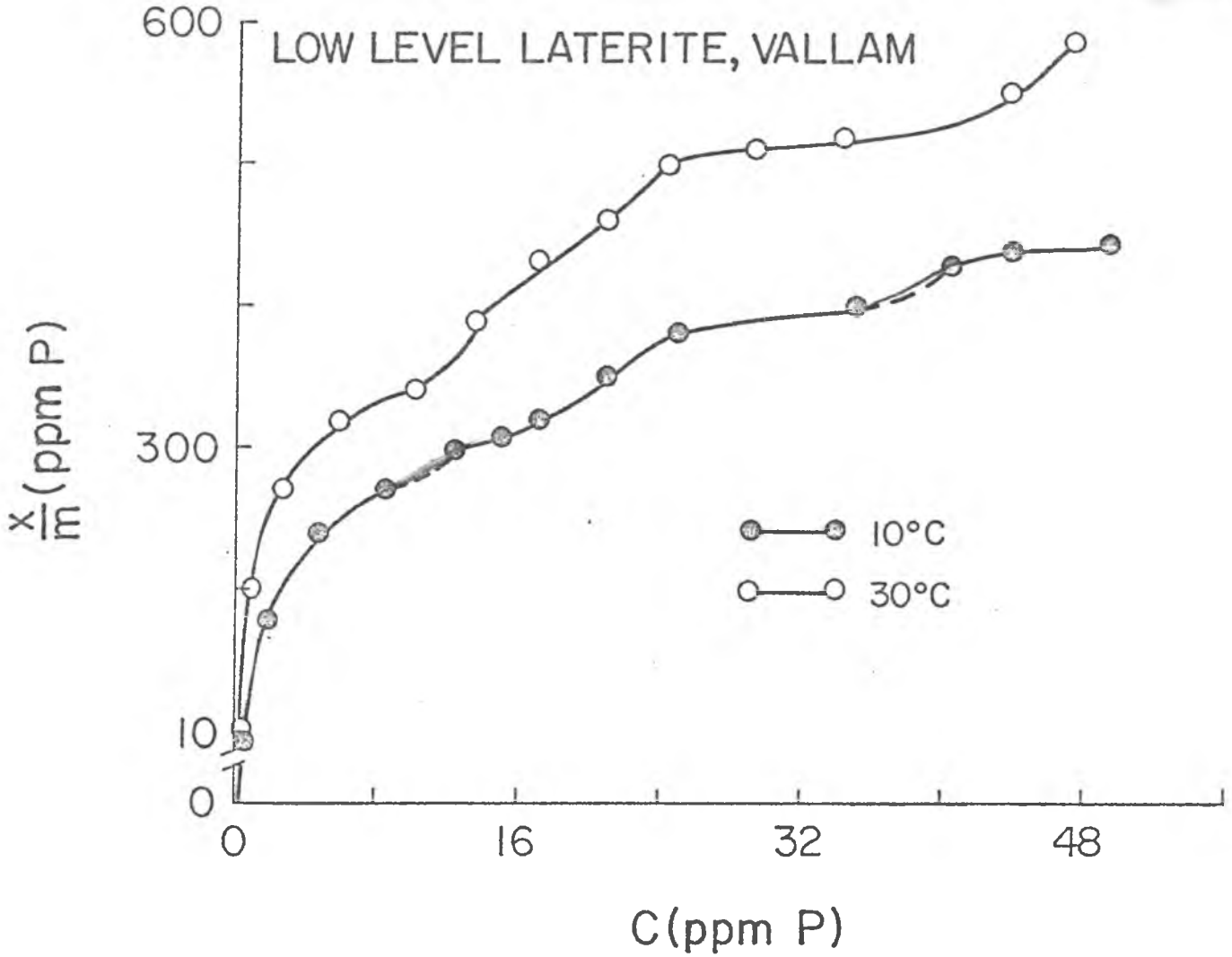


Fig. 35-Effect of temperature on P adsorption by a Low Level Laterite at a wide P concentration range (6 days equilibration in 0.01 M $CaCl_2$)

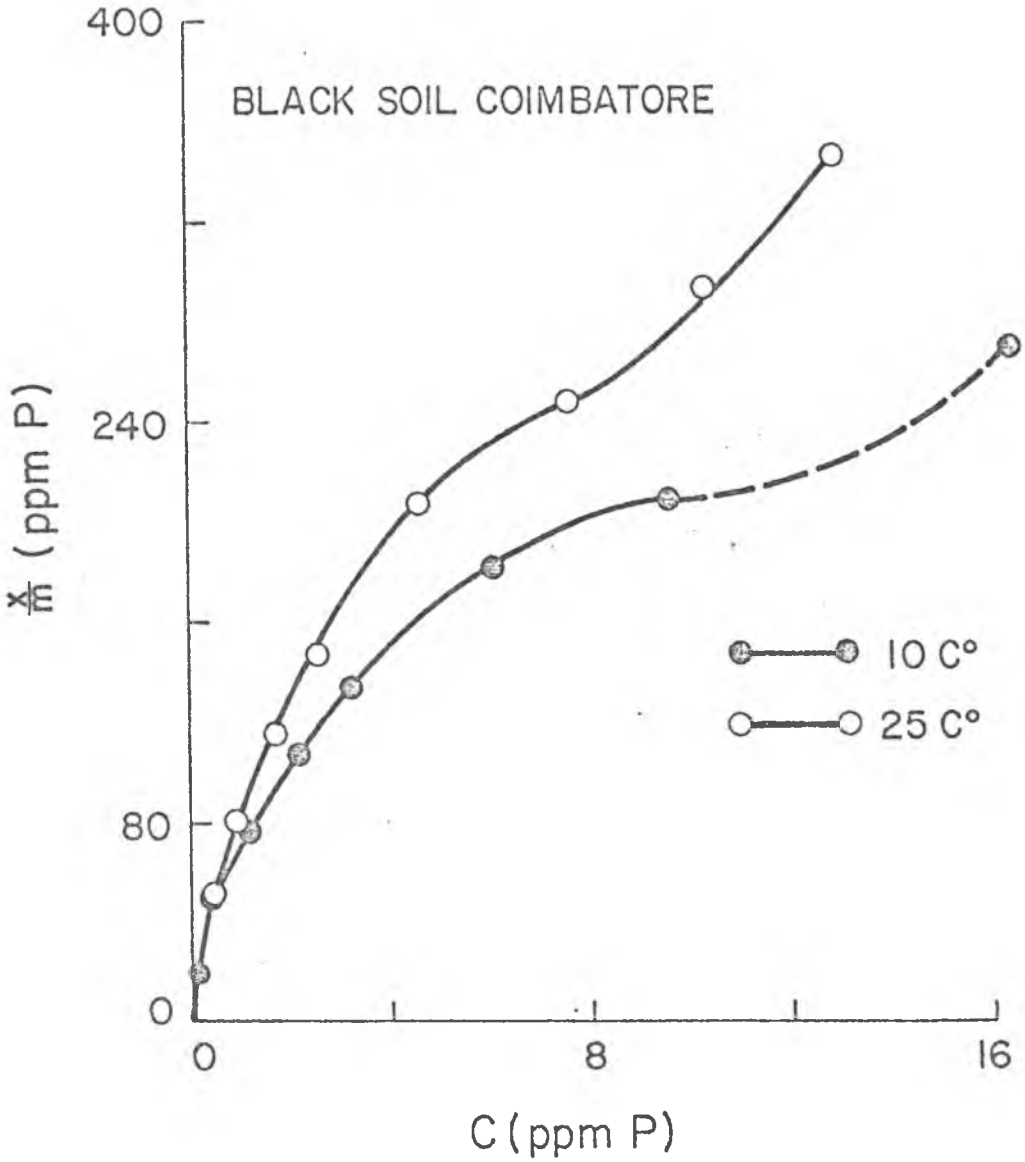


Fig. 36-Effect of temperature on P sorption by the Black soil, Coimbatore (8 days equilibration in 0.01 M $CaCl_2$ medium)

$$\Delta F = \Delta H - T\Delta S$$

where

ΔF = change in the free energy

ΔH = change in the heat of adsorption

T = temperature

ΔS = change in entropy

According to the above equation the ΔS should be positive for the ΔF to be a negative value.

Since the isotherms were constructed at more than one temperature it was possible to calculate the "isosteric heat" of P adsorption. This quantity can be defined as the "differential heat of adsorption when the amount of adsorbate is kept constant." This can be estimated by applying the Clausius equation to the adsorption data as described in the 'Materials and Methods' section. Whenever the isotherms are determined at three temperatures, there exists three possible ways of calculating the heat of adsorption using the equation. In the present study, calculations made in a similar manner gave the $\overline{\Delta H}_{x/m}$ values in close agreement (Appendix Table 11). For comparing the heat of adsorption values with other soils where only two temperatures were used, it was decided to use the $\overline{\Delta H}_{x/m}$ values obtained from isotherms of 10 and 20 or 25°C. The isosteric heat of adsorption values are plotted against the fractional surface coverage, referred as θ in Figure 37.

To calculate the fractional surface coverage (θ) values it is necessary to know the total P reactive surface available for adsorption. Three ways can be suggested to estimate the total surface (σ) (i) measurement using ethylene glycol, (ii) calculation from P

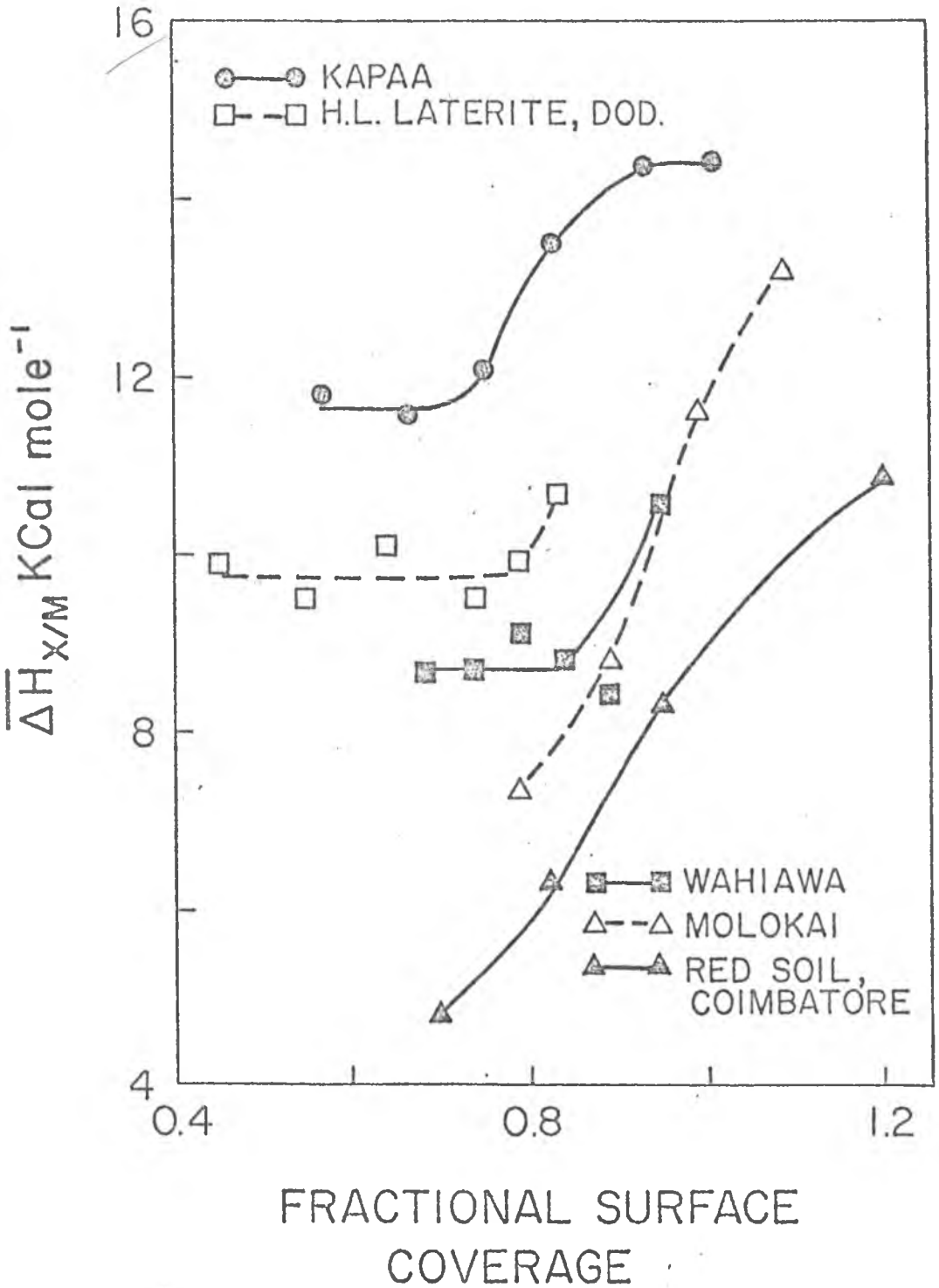


Fig. 37-Isosteric heat of P adsorption plotted as a function of fractional saturation of primary P reactive sites in five soils

adsorption data using the Langmuir's equation, (iii) by determining P adsorption at very close intervals and locating the point of completion of P adsorption on the layer of primary sites which corresponds to the "knee" of the isotherm (Adamson, 1960). Olsen and Watanabe (1957) have shown that adsorption maximum determined following Langmuir equation gave good estimates of surface area and the values were closely correlated with those obtained using ethylene glycol. Unless the observations in the isotherm are close, it may not be always possible to locate the x/m value of monolayer saturation of P reactive sites directly from the adsorption plot. In the present case, the Langmuir adsorption maximum was used as an estimate of maximum adsorption for saturation of P reactive sites. As established in another section (Fig. 15), the observed and calculated monolayer x/m values (b_{max}) gave close agreement, which adduce another justification for using the b_{max}. The isotherm determined at 20 or 25°C was used for this calculation. Though Clausius equation assumes constant amount of surface available for adsorption, as criticized by many authors it is contrary to experimental facts. The increase in T gives higher b_{max}, due either to creation of new sites and/or to multilayer P adsorption. Since 25°C approximates room T, isotherm of this T was chosen.

First the θ (fractional surface coverage) values were obtained by dividing x/m by σ (surface area). However, on plotting $\overline{\Delta H}_{x/m}$ against θ the curves did not seem to be meaningful. The possible reason was thought to be omission of P already present in the adsorption sites. So another set of θ values were calculated using the equation

$$\theta = \frac{x/m + E}{\sigma}$$

Where

θ = fractional surface coverage

x/m = amount of P adsorbed

E = surface P (estimate of the labile P already present)

σ = adsorption value at saturation of P reactive sites

Figure 37 shows the increase in $\overline{\Delta H}_{x/m}$ after a fractional P reactive surface coverage of about 0.75. The variation in $\overline{\Delta H}_{x/m}$ may be accounted for by molecular interaction and surface heterogeneity (Everette, 1950; Tompkins, 1950). Considering the soil surface the contribution by non-uniformity of the surface is likely to be important. Thus after saturation of certain fraction of the P reactive sites another group of sites which were less energetic and requiring higher heats for adsorbing P might have dominated the system.

The "Equilibrium Phosphate Potential"

The "equilibrium phosphate potential" is obtained by plotting the phosphate potential values (1/2 pCa + pH_2PO_4) against P gained or lost and by extrapolation or interpolating to $\Delta P = 0$. The data for contrasting Hawaii and Indian soils is presented in Figures 38 and 39 show that this procedure of interpolating was not applicable for these soils as the curves tended to stay near the point of zero ΔP because these tropical soils have a tremendous capacity to sorb P even at low solution P concentrations.

The phosphate potential values obtained for the 8 Hawaiian and 8 Indian soils are presented in Appendix Table 12. In estimating the phosphate potential value it is usually assumed that calcium activity in solution remains the same, roughly 0.01 M. But, as presented in the

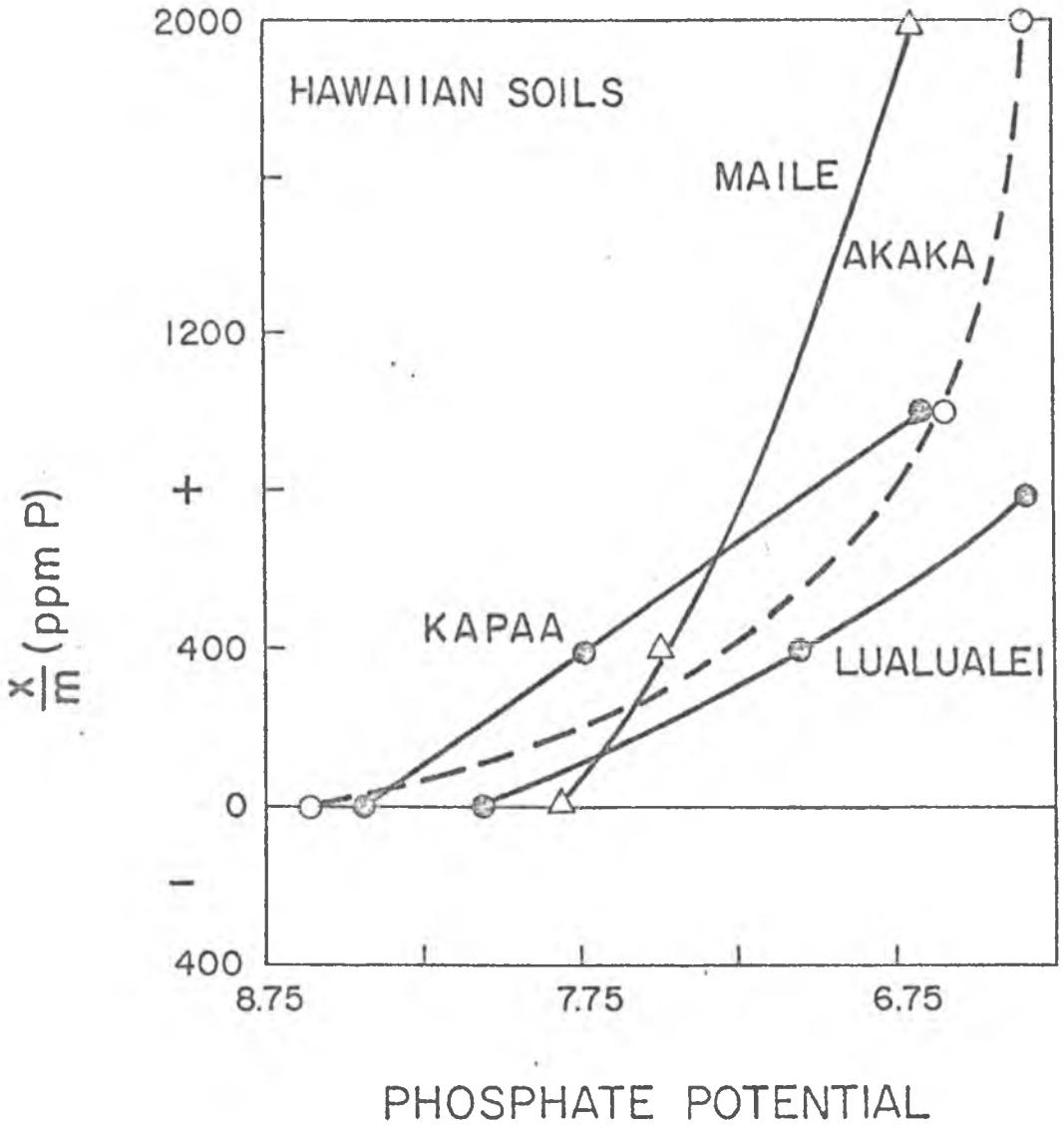


Fig. 38-Amount of P gained or lost (+ or - x/m) plotted as a function of phosphate potential in four Hawaiian soils (30 minutes equilibration)

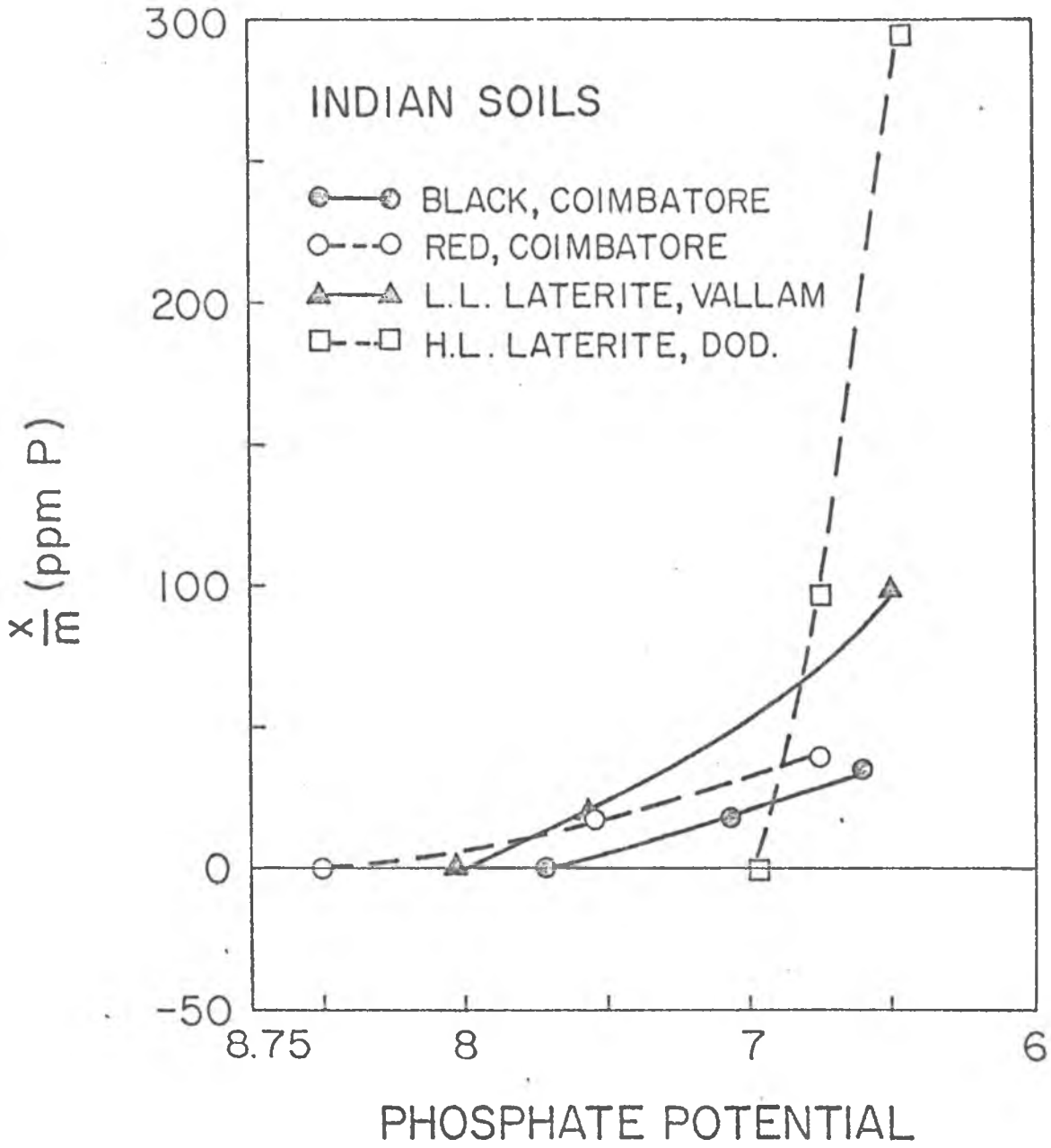


Fig. 39-Amount of P gained or lost (+ or - x/m) plotted as a function of phosphate potential in four contrasting Indian soils (30 minutes equilibration)

Appendix Table, this assumption may not hold good for all soils. In the present study the calcium concentration in the equilibrium solution where no P was added ranged from 288 (0.0072 M, Lualualei) to 400 ppm (0.01 M, Hanipoe). Since phosphate potential is 1/2 pCa + pH_2PO_4, the difference in the activity of calcium can introduce great error if it is not accounted for.

The second assumption is that the calcium potential is much less variable than phosphate potential. This means that soil has little influence on calcium concentration of the equilibrating solution when one shakes the soil with 0.01 M $CaCl_2$ (Russell, 1961). Results obtained here indicate that this assumption is also not valid. The concentration of P in solution here was less than 0.02 ppm at $\Delta P = 0$. So the phosphate potential values obtained may reflect calcium activity more than that of P. These observations lead to the conclusion that the phosphate potential values of soils which are highly P adsorptive, and widely different in their chemical properties, especially in relation to calcium content, may not be meaningful. This is in partial agreement with a report of White and Beckett (1964).

Desorption of Phosphorus

P desorption isotherms constructed for Lualualei, Wahiawa and Akaka soils are present in Figures 40 and 41. Hysteresis was observed for all soils - the magnitude being greatest for soils of high P adsorption capacity. Similar observations have been made by other researchers (Kafkafi, et al., 1967; Fox and Kamprath, 1970). The significance of the hysteresis effect is that it may render the predicted P supply patterns of soils unrealistic in terms of absolute basis. One obvious

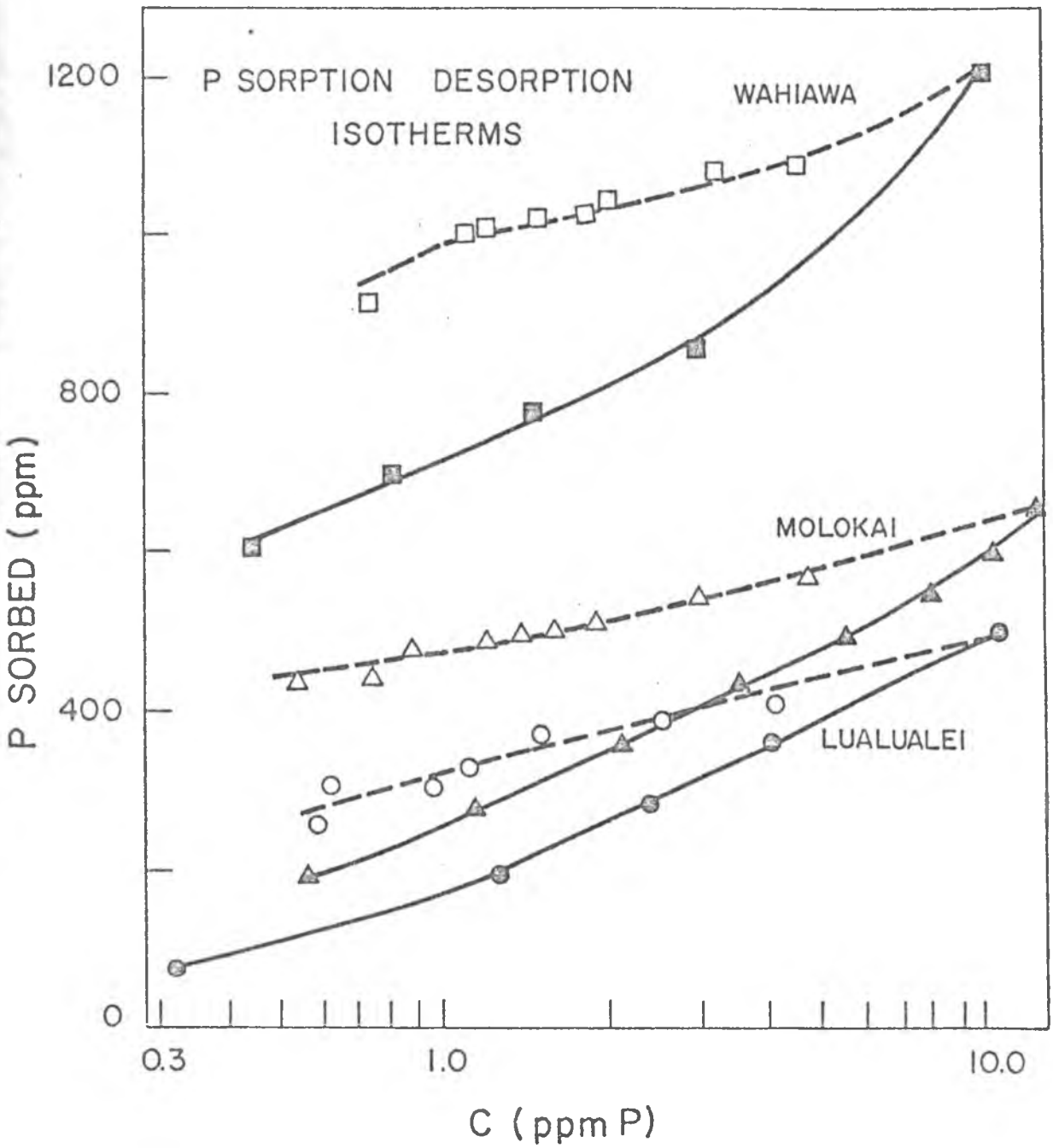


Fig. 40-P adsorption (solid line) and desorption (broken line) isotherms of three Hawaiian soils (6 days and 4 hours equilibration for adsorption and desorption respectively. Ionic environment - 0.01 M $CaCl_2$)

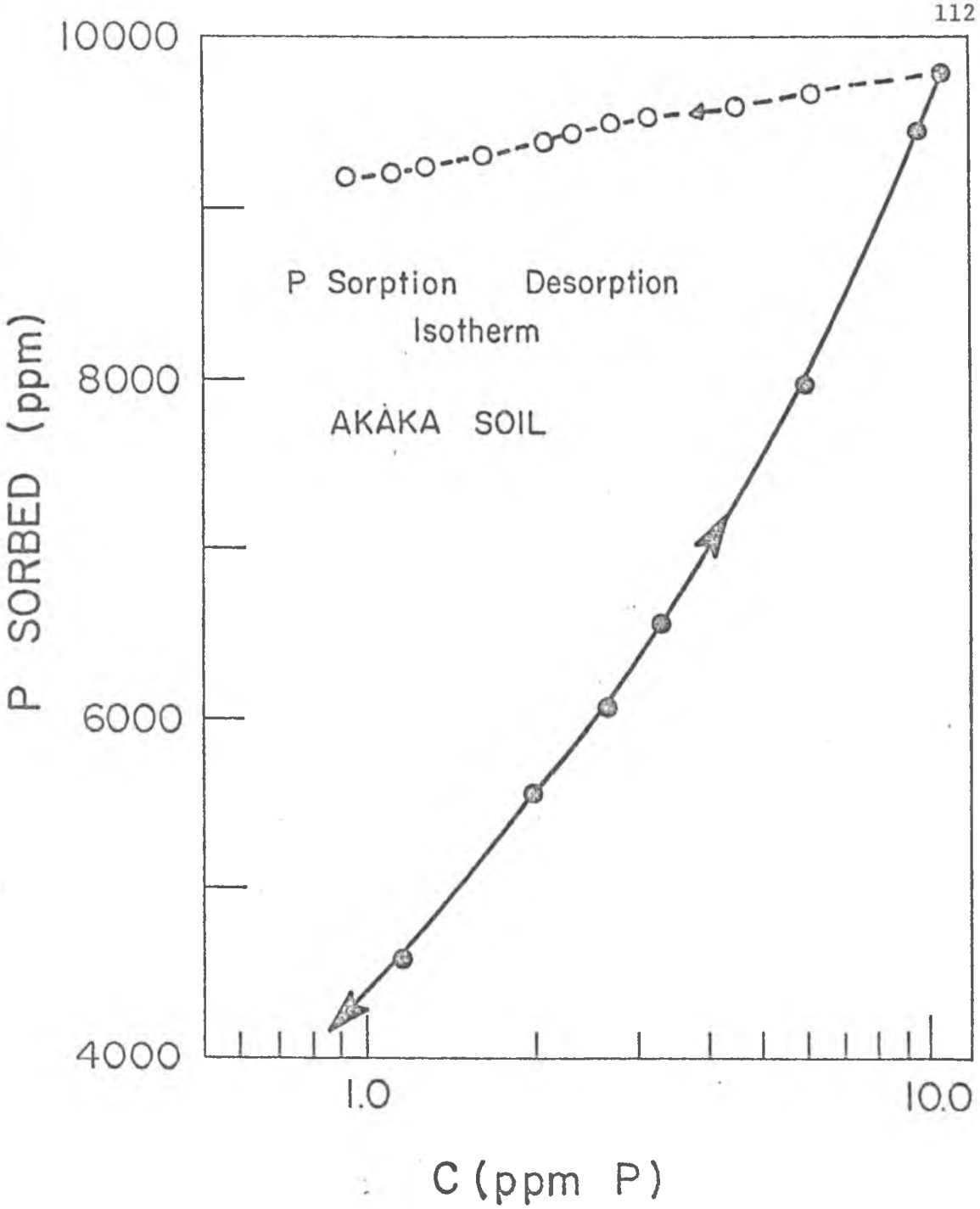


Fig. 41-P adsorption (solid line) desorption (broken line) isotherms of Akaka soil (6 days and 4 hours equilibration for adsorption and desorption respectively. Extractant - 0.01 M $CaCl_2$)

reason for the hysteresis is the difference between specific adsorption of phosphate and non-specific adsorption of chloride. The latter was the mechanism of desorption and was relatively ineffective. In addition, on more and more extraction of soil with 0.01 M $CaCl_2$, more silicon also will be leached from the soil. This may result in creation of additional sites for P adsorption.

Although the results of desorption experiments using 0.01 M $CaCl_2$ may not be altogether meaningful in absolute terms the data should indicate the relative P supply behavior of soils.

The equilibrium P concentration plotted against the volume of extractant used is illustrated in Figure 42. The results are in accord with a report of Fried and Shapiro (1956) and Vaidyanathan and Nye (1970). The P release patterns of Molokai, Wahiawa and Akaka soils are like desorption. In Lualualei the probability is for dissolution of calcium phosphate precipitates ($CaHPO_4.2H_2O$ and Apatites) instead of desorption. The resemblance of P release curve to desorption mechanism can then be ascribed to the nature of surface controlled dissolution of the precipitates (Dietz, et al., 1964; Marshall and Nancollas, 1969). To start with all the soils had roughly the same P concentration in solution. However, on desorption Akaka maintained higher P concentration in solution than the other soils used. For example at a soil:solution ratio of 1:400, the solution concentrations of P were 0.59, 0.54, 0.73 and 1.23 ppm in Lualualei, Molokai, Wahiawa and Akaka soils respectively. The above data clearly reflects on the varying capacities of the soils to maintain the P content of solution (P buffering capacity).

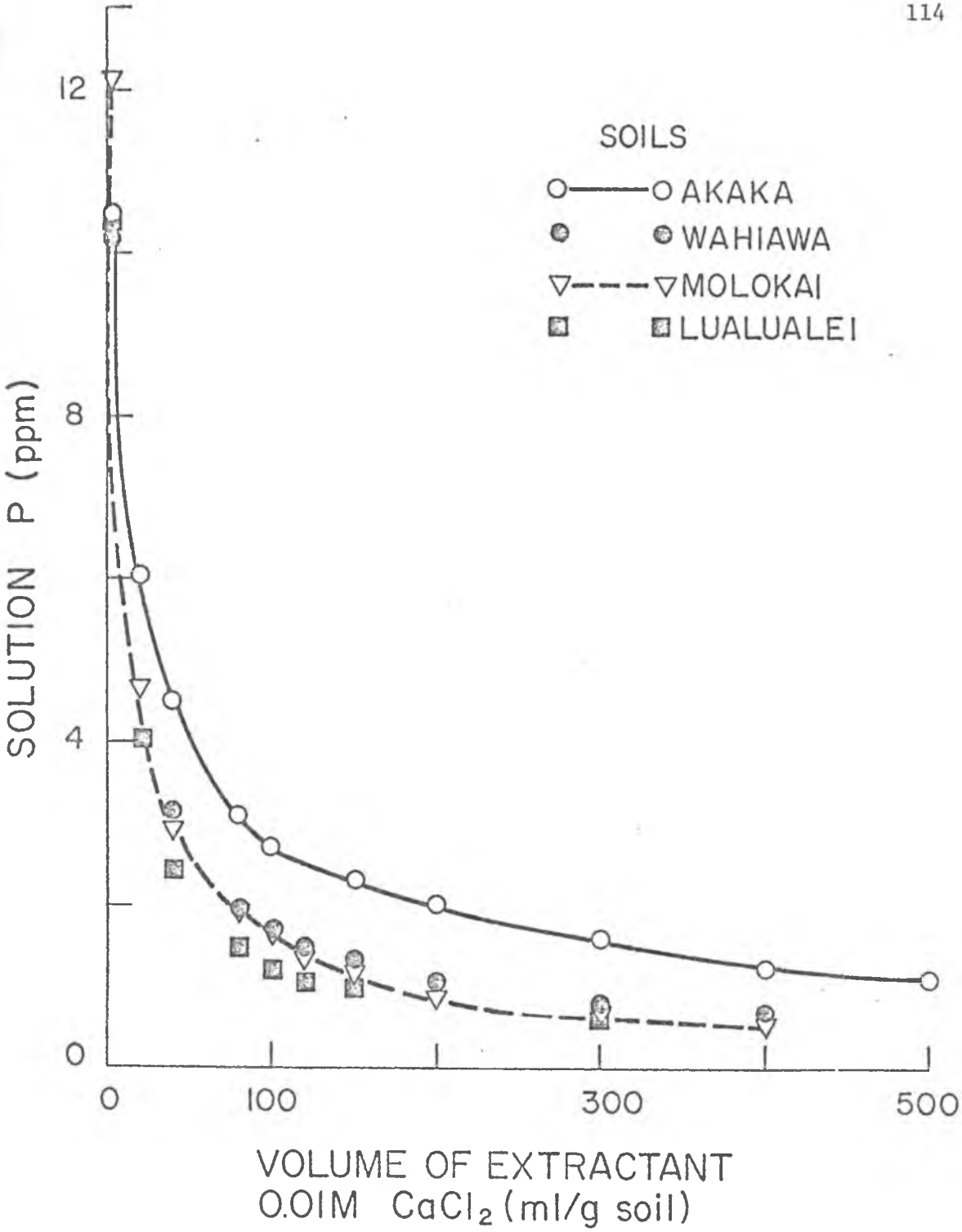


Fig. 42-P remaining in solution on extraction of four Hawaiian soils with 0.01 M $CaCl_2$ solution (Extraction time 4 hours)

Studies on Phosphorus Availability to Plants

A greenhouse experiment was mainly undertaken to study the relationships between adjusted P concentration in soil solution and crop yields and P uptake by millet. Phosphate sorption isotherms, constructed for eight Hawaiian and four Indian soils, from data obtained by the standard procedure, are presented in Figures 43 and 44. The vertical lines in the figures indicate adjusted solution P concentrations chosen for growing plants in pots.

The isotherms show a tremendous variation in P sorption by the soils, especially those collected from Hawaii. Similar results were obtained by Fox, et al. (1968, 1971). Ozanne and Shaw (1968) suggested that the amount of P adsorbed, as P concentration increased from 0.25 to 0.35 ppm, may serve as a good measure of the capacity of the soil to continuously renew soil solution with that nutrient. The adsorption maximum calculated using the linear form of the Langmuir equation also can give an estimate of the capacity factor.

The buffering capacity values calculated by both methods are summarized in Table 12. Use of the slope between solution concentrations of 0.25 and 0.35 ppm was found to give unrealistic values for some soils. For example, values were similar for Red Soil, Coimbatore and Low Laterite, Vallam, though as the sorption isotherms indicate, the latter has much higher adsorption capacity than the former. A similar discrepancy was observed between Kapaa and Hanipoe soils also.

The P adsorption capacity of soils arranged according to their mineralogy is as follows: montmorillonite clays (Black Soil) < kaolinite (Molokai, Wahiawa and Red and Laterite Soils from India) < x-ray

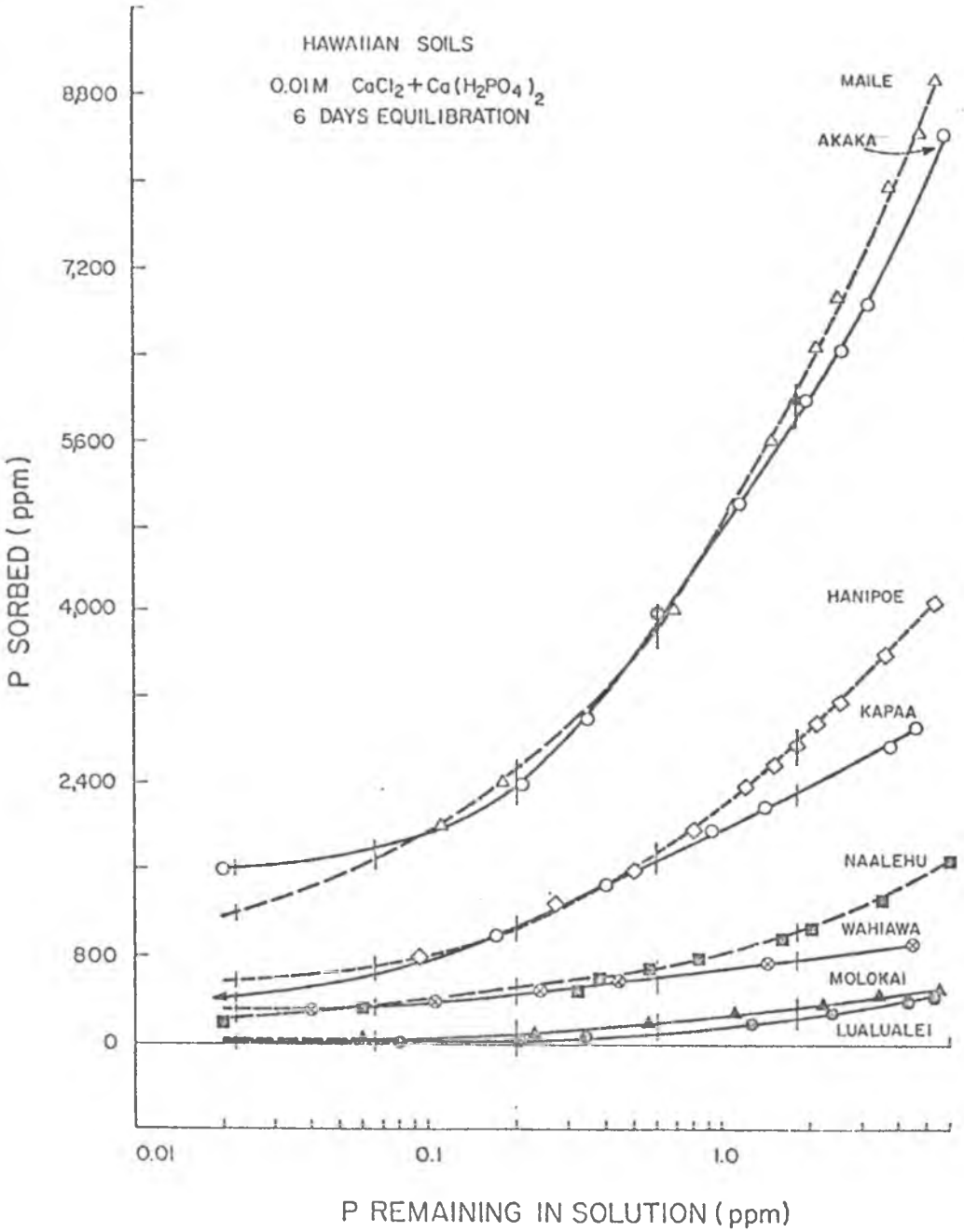


Fig. 43-Phosphorus sorbed by eight Hawaiian soils in relation to P in the equilibrium solution

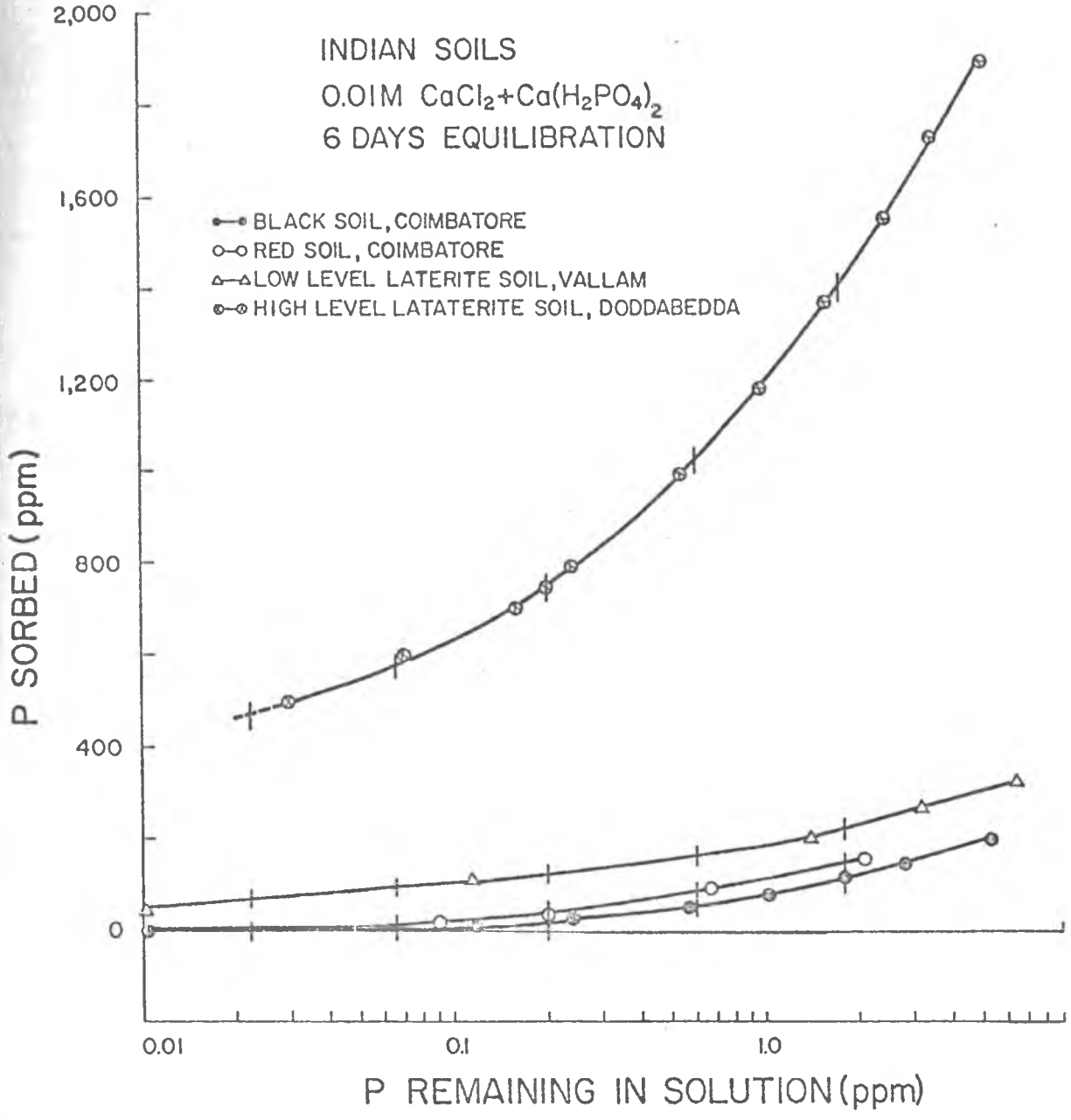


Fig. 44-Phosphorus sorbed by four Indian soils in relation to P in the equilibrium solution

Table 12. Phosphate buffering capacity of soils calculated using the slope of the P sorption isotherm between equilibrium solution concentrations of 0.25 and 0.35 ppm P and by following the Langmuir equation (b_{max})

Soil	P buffering capacity (µg/g)	
	Slope between 0.25 to 0.35	b_{max}
Hawaiian Soils		
Lualualei	22	599
Molokai	45	566
Wahiawa	55	899
Kapaa	180	2623
Akaka	480	8000
Naalehu	75	1346
Maile	430	10506
Hanipoe	160	4464
Indian Soils		
Black Soil, Coimbatore	7	287
Red Soil, Coimbatore	13	254
Low Level Laterite, Vallam	12	394
High Level Laterite, Doddabedda	130	2221

amorphous material (Hanipoe, Maile and Akaka). Although oxides of Fe and Al are abundant in soils like Wahiawa and Molokai on one hand, and Akaka, Maile and Hanipoe on the other, the P sorption capacity is remarkably higher in the second category. This can be attributed to the enormous surface area exhibited by the amorphous materials present in these soils, in comparison with the well crystallized and well aggregated materials of the Wahiawa and Molokai soils. In addition, high adsorption by Akaka soil can be accounted for by the presence of a high proportion of more reactive "hydroxo" groups compared to the "oxo" groups that dominate the surfaces of Wahiawa and Molokai soils. The Lualualei soil has a high capacity for P adsorption also. This is due to the presence of large amounts of gypsum and carbonates of Ca and Mg which react with P applied, forming sparingly soluble calcium phosphate compounds.

Millet yields in relation to adjusted levels of P remaining in solution of Hawaii soils are presented in Figure 45, and for Indian soils in Figure 46. The response curves show that the 95 % yield values for the several soils were obtained at three solution P concentrations (0.022, 0.066 and 0.6), depending on the adsorption capacities of the soils.

The P adsorption maximum calculated using the Langmuir's equation, and the amount of P applied to raise the equilibrium solution concentrations to the required levels, enabled calculation of the percentage saturation of the adsorption maximum at different rates of P application, as indicated below.

$$\text{P Percentage Saturation} = \frac{\text{Amount of P applied} + E}{b_{max}}$$

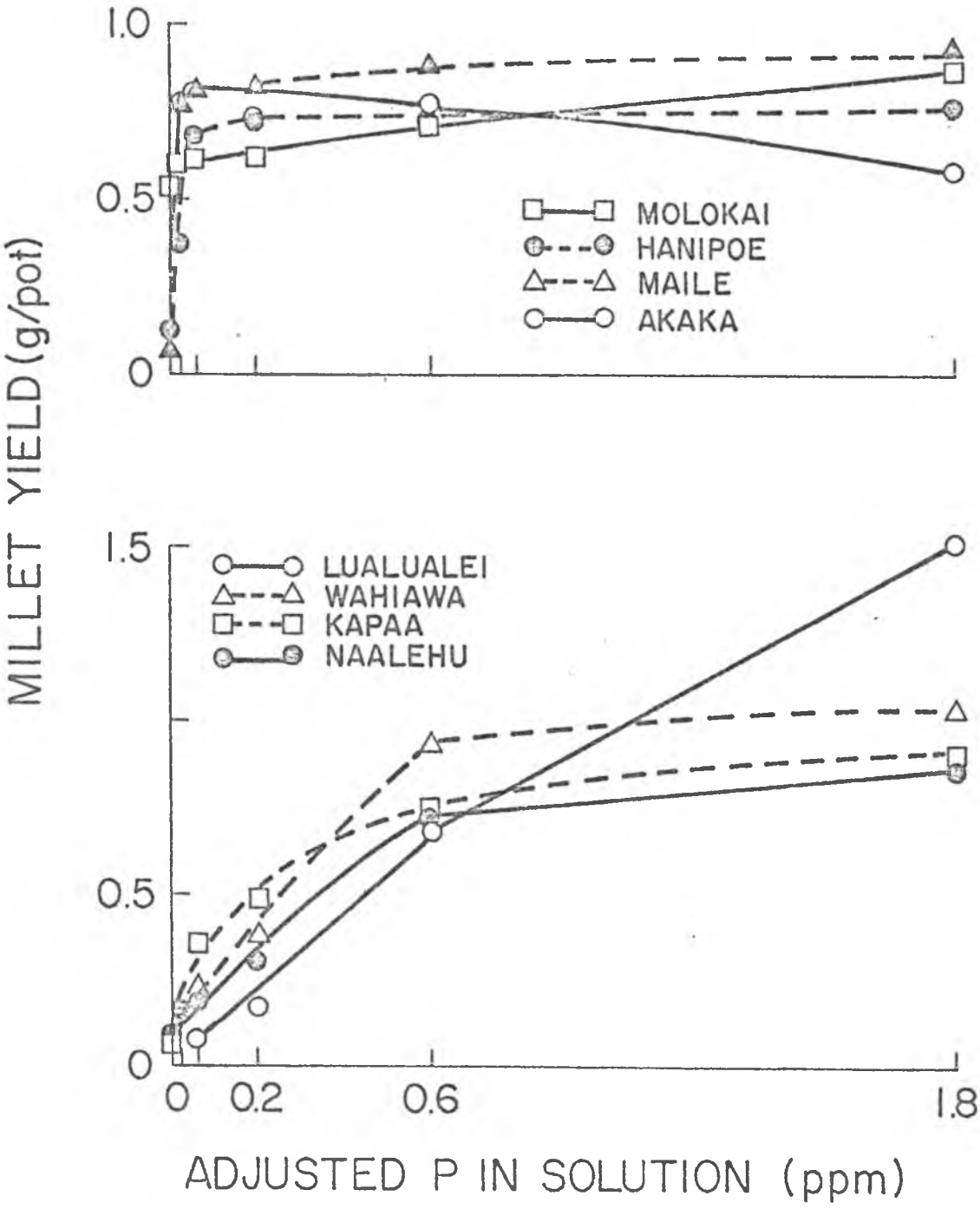


Fig. 45-Millet yields in relation to five adjusted levels of P in the soil solution of eight Hawaiian soils

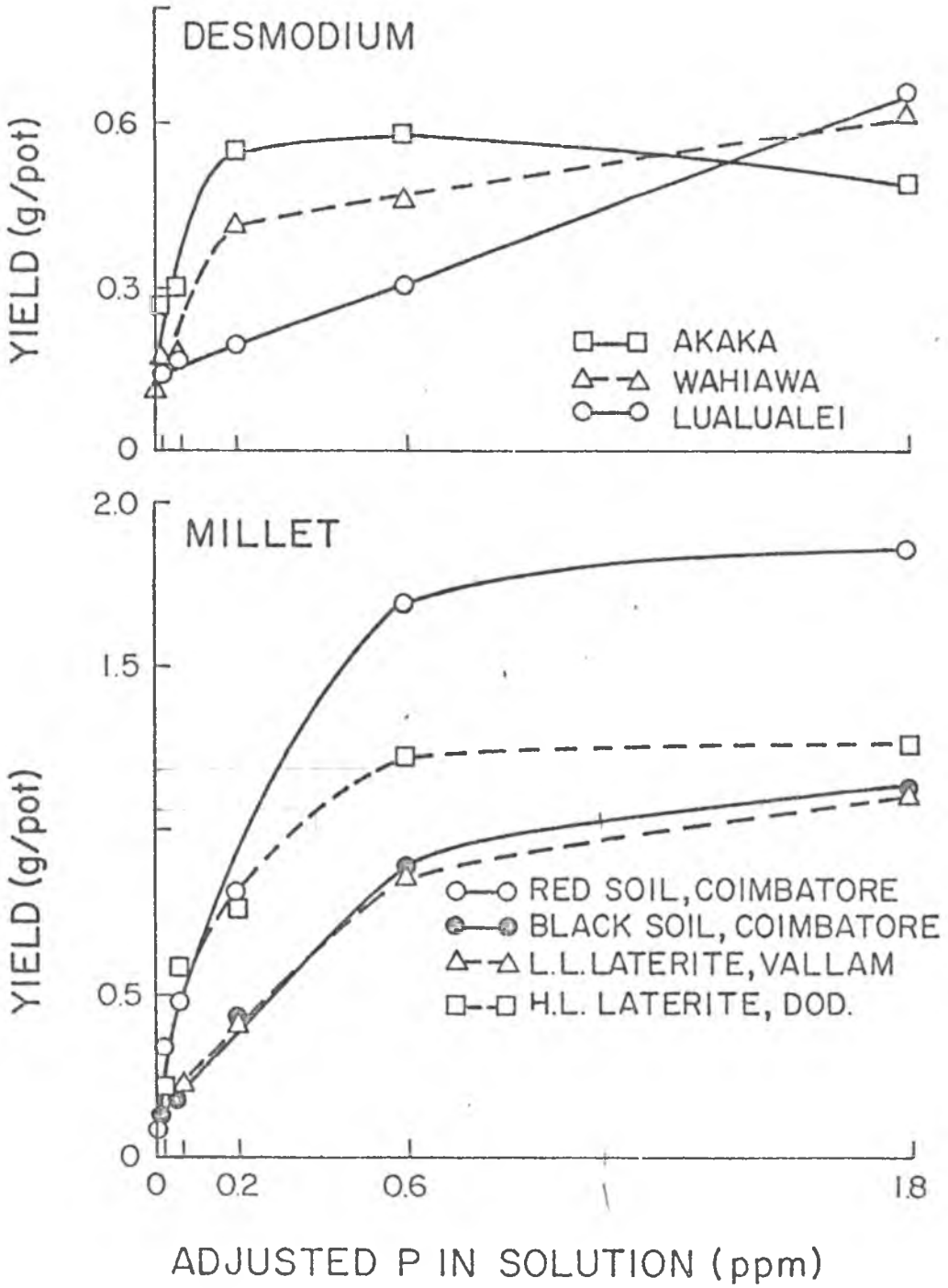


Fig. 46-Yields of Desmodium and millet as releated to five adjusted levels of P in soil solutions of three Hawaiian and four Indian soils

ere

E = Surface P estimated in the laboratory using P^{32}

b_{max} = P adsorption maximum calculated using the Langmuir equation

quilibrium solution P concentrations, P saturation of the adsorption aximum at 95 % yield, and the b_{max} values are presented in Table 13. lolokai soil was not included in the table as practically no response was)btained from P applications to this soil. Yield for the Lualualei soil iid not reach a plateau. A significant feature is that most of the soils required an adjusted P solution concentration of 0.6 ppm for 95 % yield in spite of their adsorption maxima ranging from 254 (Red Soil) to 2600 (Kapaa Soil). This concentration (0.6 ppm) is much higher than the values suggested by some researchers (Beckwith, 1965); Ozanne and Shaw, 1967; Fox, et al., 1968; Fox and Kamprath, 1970). One explanation is that since the experiment was conducted in pots, the soil volume available for nutrient absorption by plants was limiting. Also, the tendency of roots to "pile up" against the walls and bottoms of pots removes many roots from the soil environment, thus necessitating higher solution concentrations of P in the soil solution. However, when the P sorption capacity reached a level of about 4500 and above, the adjusted P concentration in solution required for 95 % yield was only to 0.066 ppm (Hanipoe) or even 0.022 ppm (Maile and Akaka). The percentage P saturation of soils at 95 % yield indicates an inverse relationship between this parameter and the adsorption maxima (Table 13). This confirms with the earlier reports by Woodruff and Kamprath (1965).

Table 13. Equilibrium solution P concentration and the percentage saturation of adsorption maximum at which 95 % yields were obtained for millet. The adsorption maximum values are also given for comparison.

Soil	P Remaining in Solution (µg/ml)	% P Saturation of Adsorption Maximum	Adsorption Maximum
	Hawaiian Soils		
Wahiawa	0.600	72	899
Naalehu	0.600	76	1346
Kapaa	0.600	67	2623
Hanipoe	0.066	27	4464
Akaka	0.022	25	8000
Maile	0.022	25	10506
	Indian Soils		
Black Soil, Coimbatore	0.6	24	287
Red Soil, Coimbatore	0.6	24	254
Low Level Laterite, Vallam	0.6	60	394
High Level Laterite, Doddabedda	0.6	52	2221

For soils which adsorb relatively low amounts of P, the plant phosphorus content plotted against the adjusted levels of P concentration in the soil solutions, shows the same trend as for yield response curves (Figures 47, 48). However, the behavior of high P fixing soils, Hanipoe, Maile and Akaka were different. Millet yields and P content of plants are plotted against pool phosphorus of soils (Labile P + Fertilizer P added) in Figures 49 to 52. A notable feature of these curves is that the initial increments of P added to some soils (Wahiawa, Naalehu, Kapaa and all the Indian soils) did not increase yields proportionately. Thus the yield curves are concave upward in this region. This is in agreement with the response curves obtained by Thompson, et al. (1960) and Fox (1971). In high P fixing soils like the Maile and Akaka and, to a lesser extent, Hanipoe a proportionate increase in yield was obtained even at the lowest levels of P applications. This may be accounted for by localized depletion of P near roots, in soils of low P buffering capacity. The critical plant P content for millet as grown in pots here seems to be about 0.6 % (Figure 53). Only in two instances did millet contain more than 0.8 % P. Thus there was no appreciable luxury consumption.

The adjusted soil solution concentration of P required for substantial growth may vary with different crops. For some plants 0.03 ppm P in nutrient solution may be enough (Asher and Loneragan, 1967), whereas 0.2 ppm or even more may be required for others (Beckwith, 1964; Lewis and Quirk, 1962). So in the present case an attempt was made to determine the adjusted P concentration in soil solution required for a dicot (Desmodium intortum) in comparison with a monocot (millet). Three

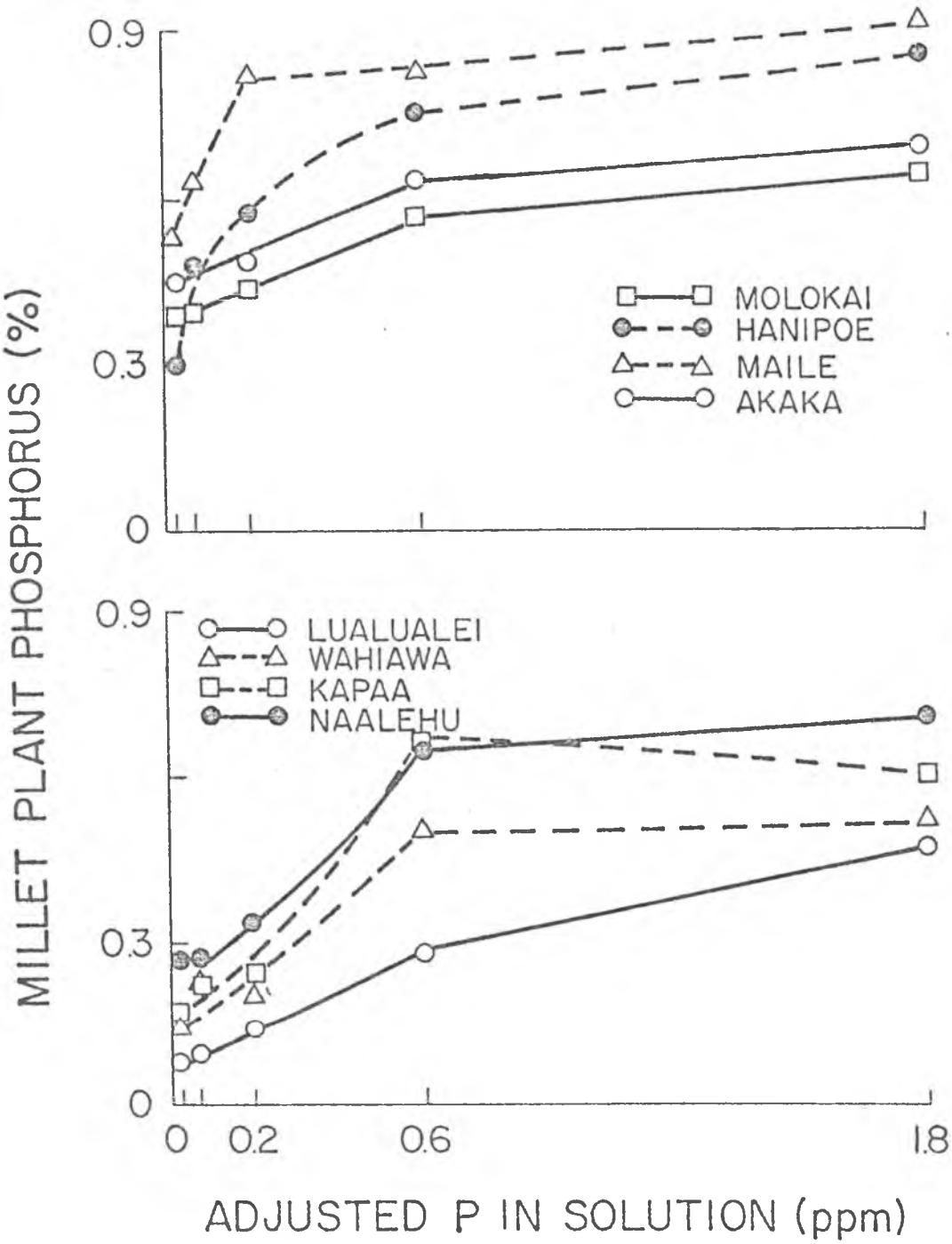


Fig. 47-The phosphorus content of millet as related to the adjusted levels of P in soil solutions of eight Hawaiian soils

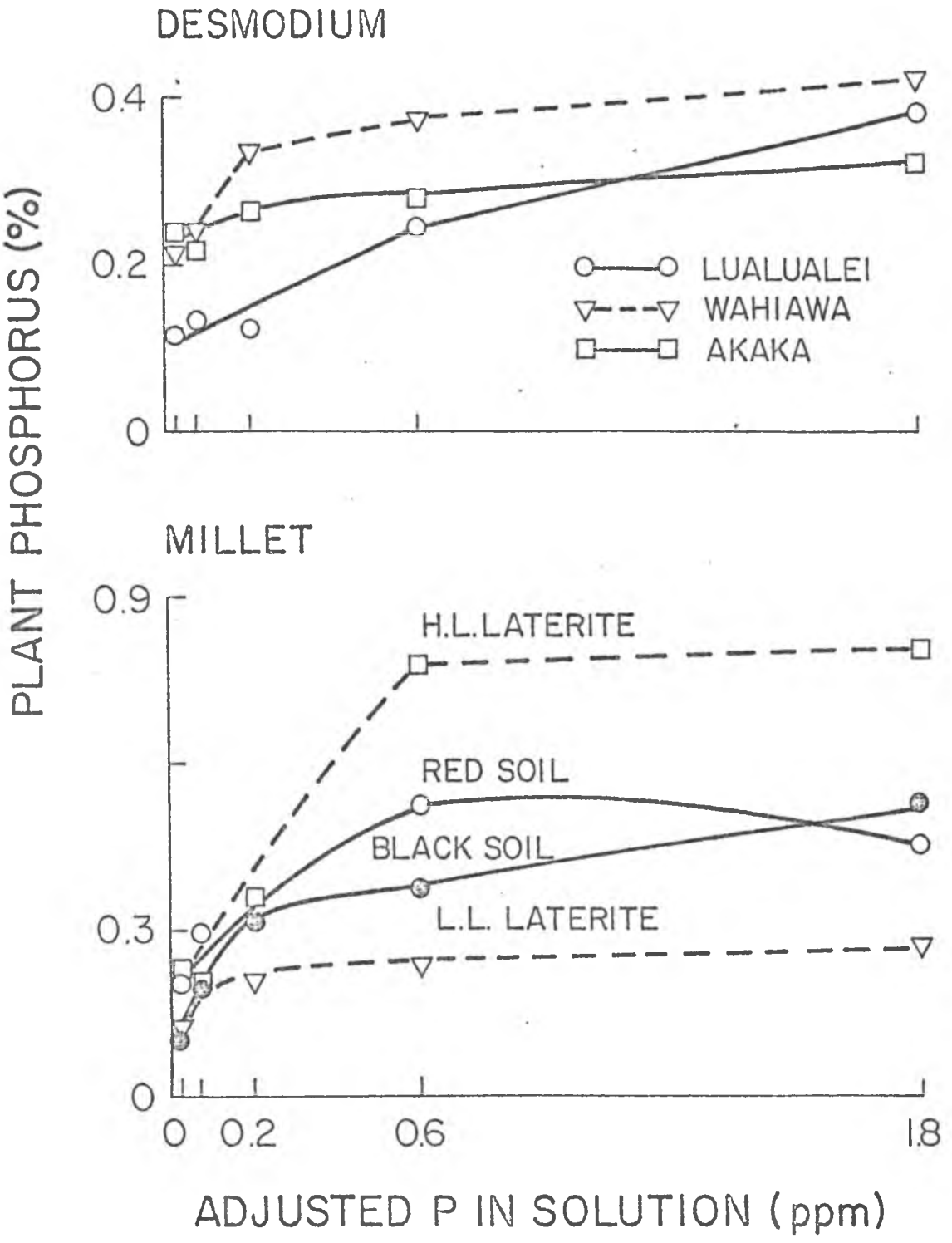


Fig. 48-The phosphorus contents of Desmodium and millet as related to adjusted levels of P in soil solutions of three Hawaiian and four Indian soils

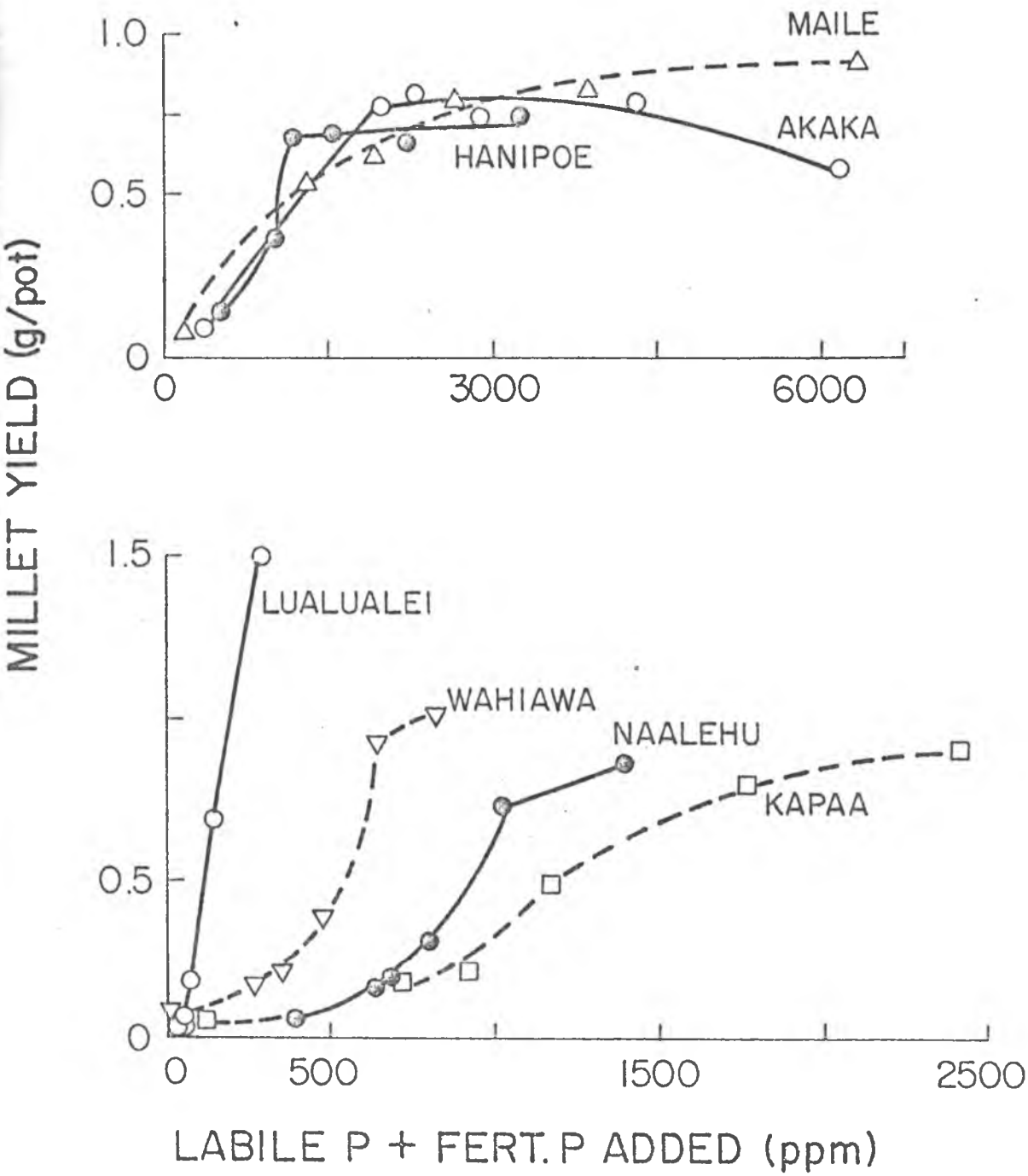


Fig. 49-Millet yields as related to the pool phosphorus (labile P + fertilizer P added) in seven Hawaiian soils

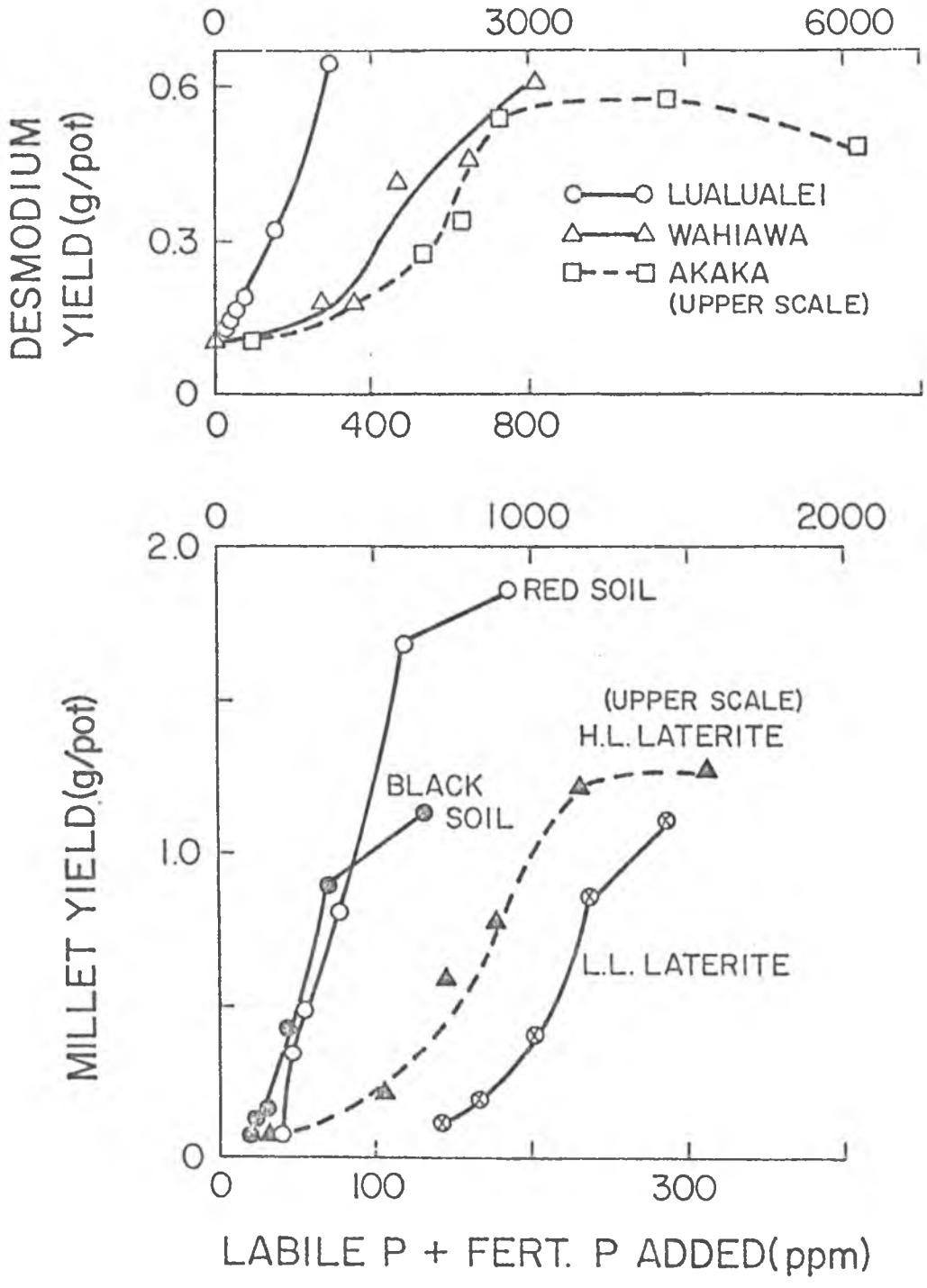


Fig. 50-Desmodium and millet yields in relation to the pool phosphorus (labile P + fertilizer P added) in three Hawaiian and four Indian soils respectively

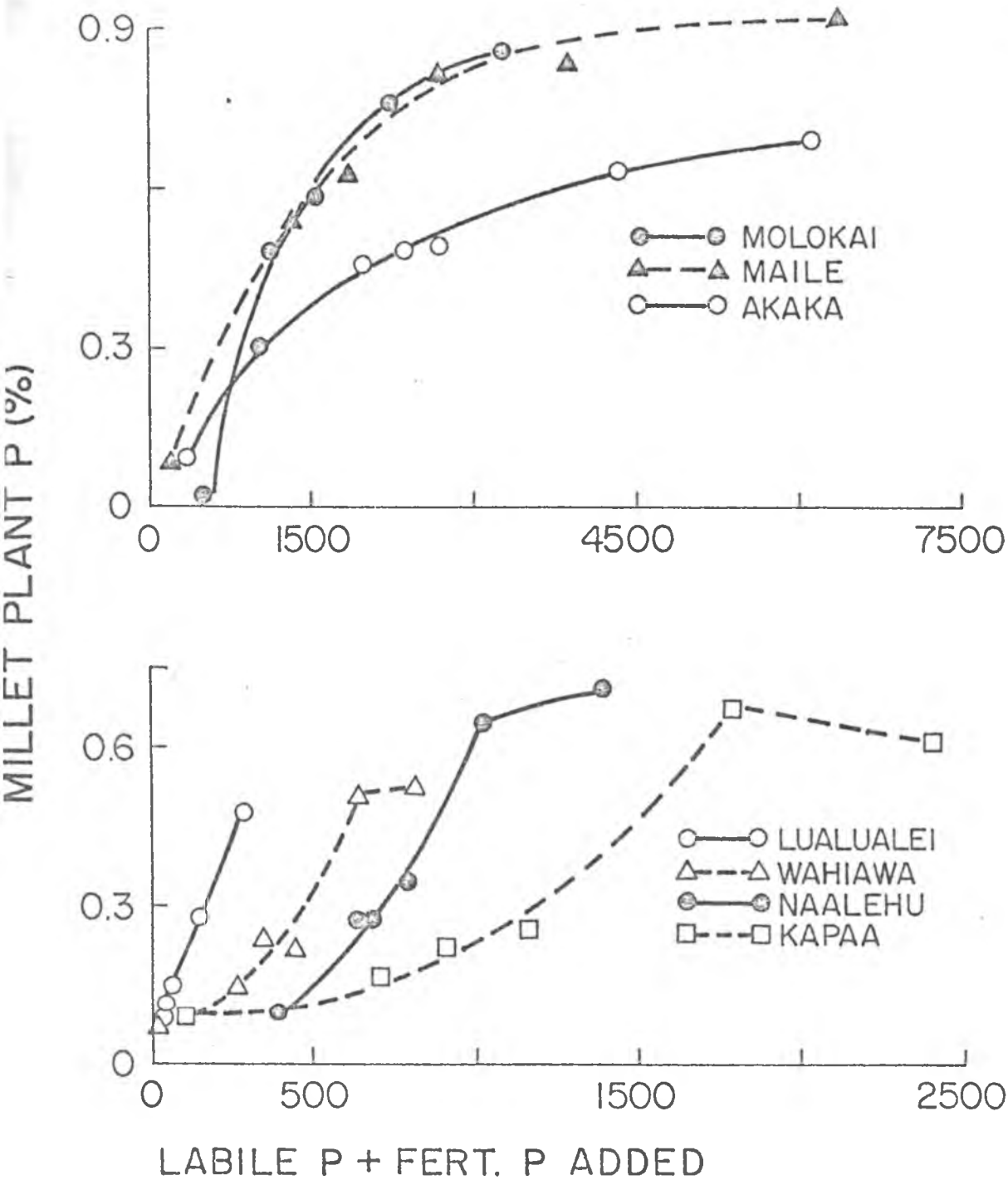


Fig. 51-The phosphorus content of millet in relation to the pool phosphorus (labile P + fertilizer P added) in seven Hawaiian soils

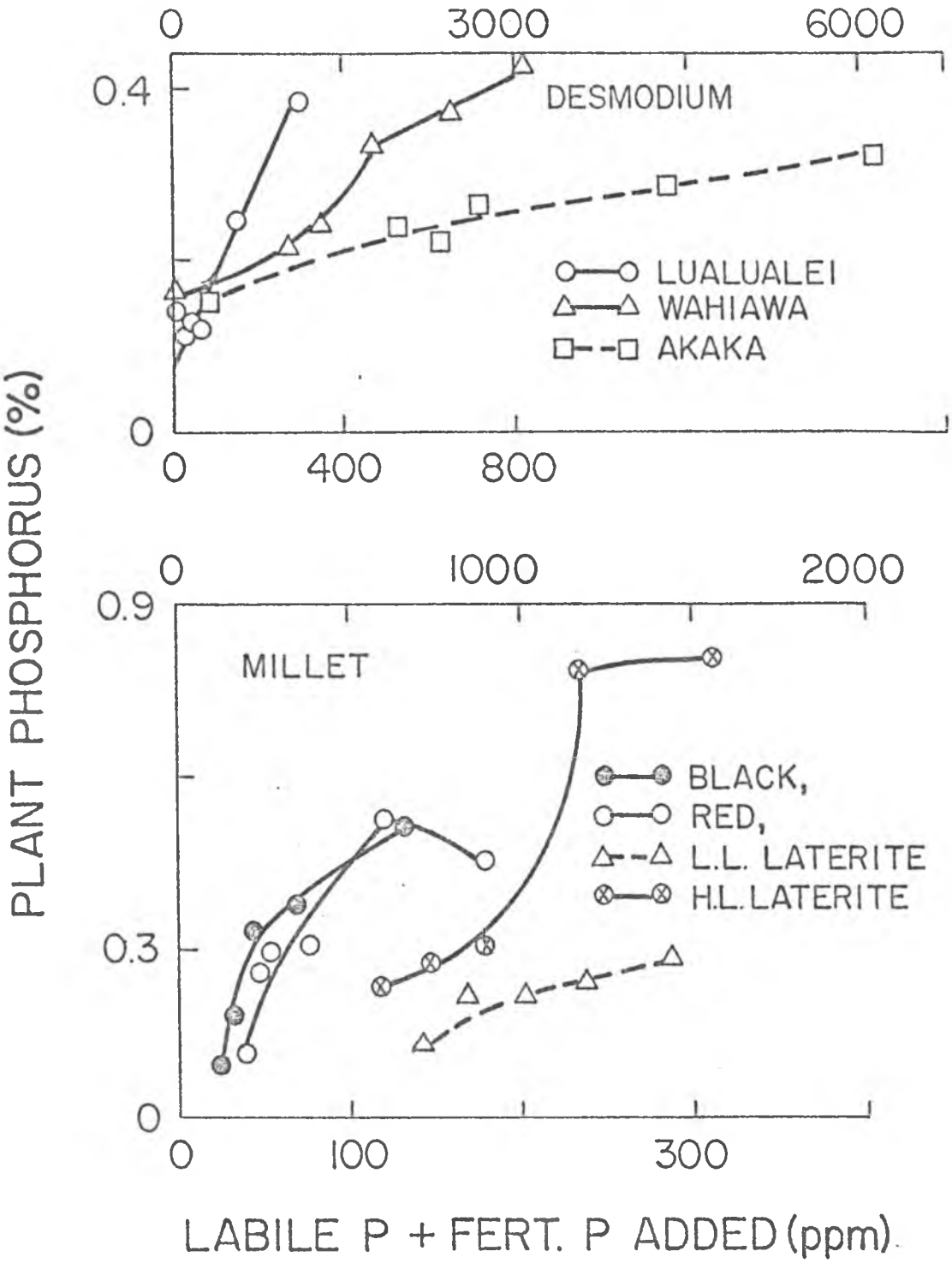


Fig. 52-The phosphorus contents of Desmodium and millet in relation to pool phosphorus (labile P + fertilizer P added) in three Hawaiian and four Indian soils

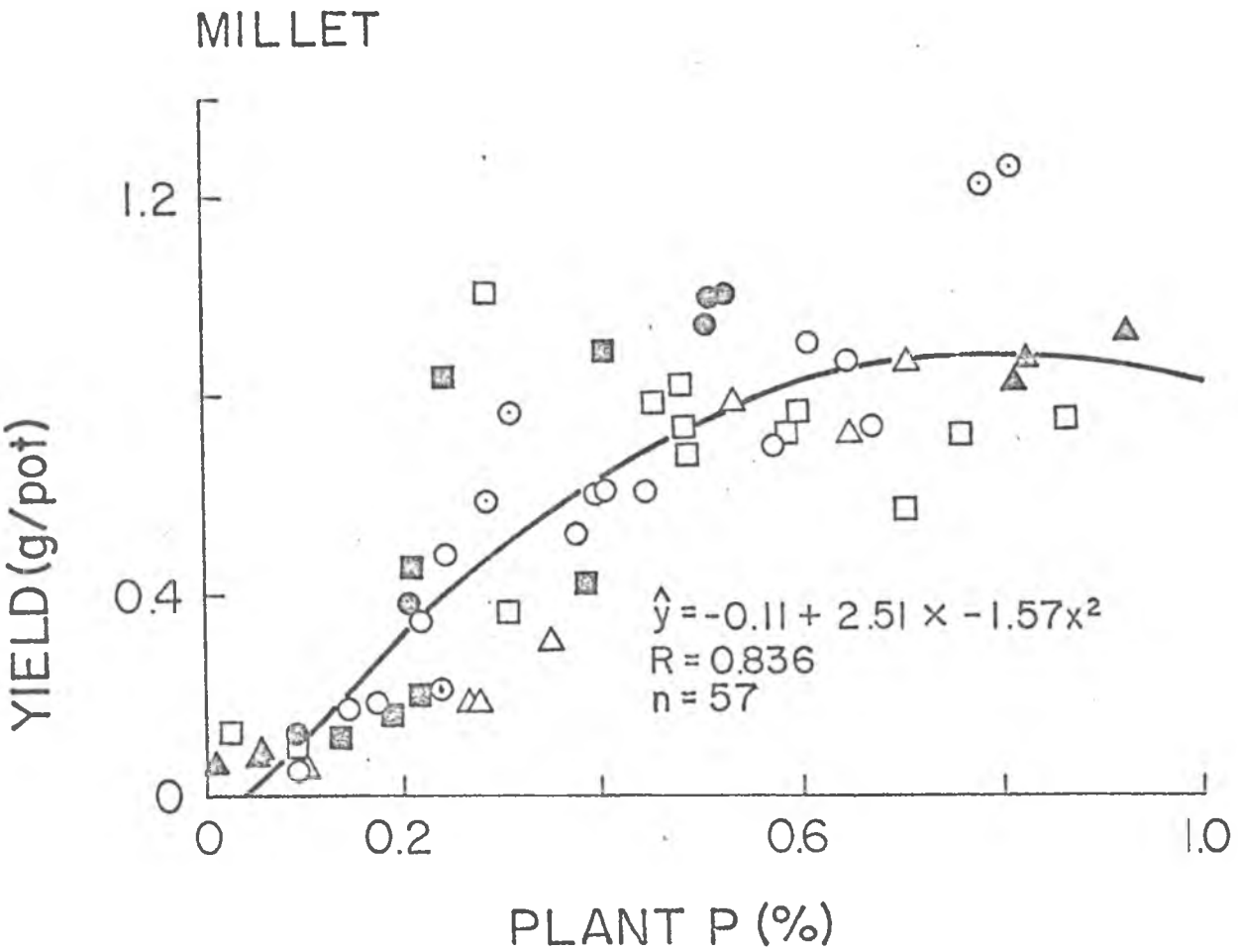


Fig. 53-Relationship between phosphorus contents and yields of millet grown on several Hawaiian and Indian soils

soils from Hawaii, Lualualei, Wahiawa, and Akaka, were chosen for this purpose. The yield response curves and P content of Desmodium in relation to P remaining in solution are presented in Figures 46 and 48. The same parameters (dry matter yield and plant P content) are plotted against pool P present in soil (Labile P + Fertilizer P added) in Figures 50 and 52. In contrast to millet, the P concentration required for 95 % yields of Desmodium was lower in Wahiawa soil (0.2 ppm compared to 0.6 ppm for millet). In Akaka, however, the value was roughly ten times higher (0.2 ppm) than for millet (0.022 ppm). This reflects the existence of interaction between crops and adjusted solution concentrations required for 95 % yields, in different soils. The Lualualei soil gave a nearly perfect straight-line response, showing a different mechanism of P release operating in this soil, perhaps an illustration of the solubility product principle as applied to calcium phosphate precipitation.

One more objective of the pot culture experiment was to find the relationship between surface P (E value) estimated in the laboratory and the L value (Labile P) as measured using millet plants at different adjusted solution concentrations. Three concentrations were tried, 0.022, 0.066 and 0.2 ppm P. The relationship between surface P and L values at different solution concentrations is illustrated in Figure 54. Only the L values, where the duplication was reasonably close, were considered in drawing the relationship between this and E values. Adjusting the P concentration in solution upward brought L values in closer agreement with surface P. Thus L values determined at 0.2 ppm P gave a better fit than the ones estimated at 0.022 or 0.066 ppm. These

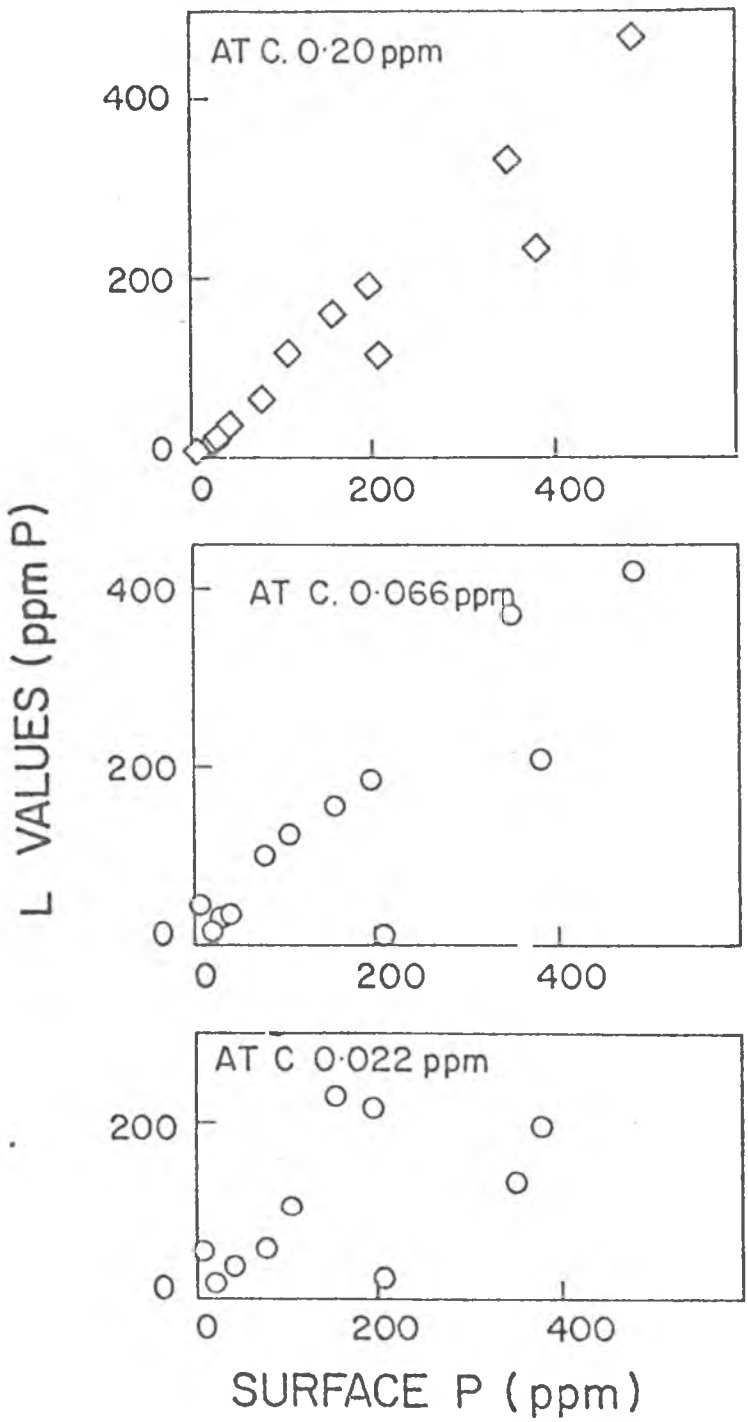


Fig. 54-L values in relation to surface P, the former estimated at different concentrations of adjusted solution P

results are in agreement with the reports of Amer (1962) and Amer, et al. (1969).

Isotopic measurement of labile P assumes that an equilibrium exists between P^{32} added, and the exchangeable native soil P. The extent to which equilibrium was attained is likely to be different under laboratory conditions compared to those in the pot experiment. It is needless to say that the E and L values will depend on the degree of equilibration existing in various soils under different solution concentrations. Apart from the physico-chemical relations in the soil, the plant physiological factor is also reflected in L value estimation (Russell, et al., 1957). In Akaka, Maile and Naalehu soils L values are less than E values and the magnitude of the difference is highest at lowest solution P concentrations. Possibly this indicates that certain fractions of P were held by these soils at a potential which made them unavailable to plants, although they remained in the exchangeable form.

SUMMARY

Adsorption of phosphorus from aqueous solutions by several Hawaiian and Indian soils was studied in relation to P concentration, equilibration time, ionic environment and temperature. Samples of a calcareous Superstition sand, collected from a pot experiment, were also included in this study to find the influence of prior P application on sorption of P subsequently added. A greenhouse experiment was conducted, in an attempt to use P sorption isotherms for evaluating P requirement of soils for optimum crop growth. Twelve soils from the Hawaiian Islands and India (Tamil Nadu) were collected and millet (Pennisetum typhoides) and Desmodium (Desmodium intortum) were grown on these soils.

To approximate equilibrium, it was necessary to allow six and eight days reaction time for acid soils and calcareous montmorillonitic soils respectively. Substitution of K for Ca in the equilibrating solution always resulted in increased P adsorption. Also an increase in the salt concentrations (KCl and $CaCl_2$) increased P retention by soils. However, the magnitude varied with soils. Taking into consideration the convenience of obtaining a clear equilibrium solution and high P concentration, 0.005 M $CaCl_2$ is recommended as equilibrating solution. For the soils investigated this concentration is more realistic than 0.01 M $CaCl_2$ generally used, as it approximates the calcium content of soil solutions.

Phosphate sorption isotherms suggested that, for non-calcareous soils at low solution P concentrations, P sorption was limited mostly to monolayer adsorption by P reactive sites. At higher concentrations an abrupt increase in P retention occurred. The shape of the isotherms

gested either the presence of groups of P reactive sites which are rgetically different and/or multilayer adsorption.

In calcareous soils at low solution P concentrations the mechanism P retention seems to be adsorption, with precipitate formation,)bably $CaHPO_4$, becoming important as P concentration in solution creased. Provided the equilibration time is long, phosphorus added a calcareous soil, even in low amounts may form nuclei for ditional P precipitation.

Almost all of the P sorption isotherms fit the Langmuir equation : = > 0.996 for all soils), thus enabling the calculation of the P dsorption maximum. The desorption data also were described using this quation. This is helpful as it makes possible the prediction of olution concentrations of P at very high dilutions using the two onstants of the equation.

Temperature studies showed the P adsorption by soils is an ndothermic process. The "isosteric heat" of P adsorption ($\overline{\Delta H}_{x/m}$) was alculated for three Hawaiian and three Indian soils at various fractions f saturation of P reactive sites. The isosteric heats of adsorption aried after 0.8 fractional surface saturation.

Intensity and capacity factors were estimated in relation to vailability of phosphate to plants using P sorption isotherms. Use of angmuir's adsorption maximum was found to be a better measure of apacity factor than the increase in P adsorption between equilibrium olution P concentrations of 0.25 and 0.35 ppm.

Millet yields were 95 % of maximum yield at adjusted solution P oncentrations of 0.6, 0.066 and 0.022 ppm, when the adsorption maxima

were < 2600, 2600 to 5400 and > 5400 ppm respectively. Cultivated soils generally show P adsorption maxima of less than 2600 ppm. Hence the results obtained here suggest the possibility of arriving at a general value of adjusted solution P concentration for optimum growth of a particular crop in most of the soils. An inverse relationship was obtained between P adsorption maxima and the percentage saturation required for 95 % yield. A comparison of yield response curves of Desmodium and millet showed an interaction existing between crops and adjusted solution P concentrations required for optimum crop growth in different soils.

Appendix Table 1. Effect of concentration of two salts on pH and P concentration (C) of the equilibrium solution, and adsorption (x/m) of P, Ca and K by three soils[a]

Soil	Salt	Concentration (M/L)	P		Cations Adsorbed		pH
			C (ppm)	x/m (ppm)	K (ppm)	Ca (ppm)	
Black Soil, Coimbatore	KCl	0.001	2.36	86	28	-	8.21
		0.010	1.66	100	190	-	7.59
		0.100	1.33	106	900	-	7.30
	$CaCl_2$	0.001	2.14	90	-	-82	7.71
		0.010	1.29	107	-	1376	7.21
		0.100	1.12	111	-	6160	6.70
Wahiawa	KCl	0.001	4.46	711	-11	-	5.73
		0.010	2.69	746	56	-	5.20
		0.100	1.77	765	540	-	5.19
	$CaCl_2$	0.001	3.09	738	-	501	5.32
		0.010	1.69	766	-	1544	5.07
		0.100	1.61	768	-	8800	4.78
Akaka	KCl	0.001	5.78	4551	-153	-	4.31
		0.010	3.13	4604	-118	-	4.24
		0.100	1.31	4641	440	-	4.30
	$CaCl_2$	0.001	2.12	4625	-	610	4.05
		0.010	1.49	4637	-	2728	4.05
		0.100	1.15	4644	-	12600	3.98

[a]Equilibration - 6 days

Appendix Table 2. Detailed phosphorus adsorption data for 8 Hawaiian soils[a]

Soil	Co (µg/ml)	C (µg/ml)	x/m (µg/g)	C/x/m
Lualualei	1	0.08	18	0.0044
	2	0.20	40	0.0051
(Typic Chromustert)	3.5	0.33	70	0.0048
	10	1.28	104	0.0066
	15	2.34	283	0.0083
	20	4.04	359	0.0112
	25	5.30	444	0.0119
	30	10.35	453	0.0228
Molokai	2	0.06	39	0.00168
	5	0.23	95	0.00241
(Tropeptic Torrox)	10	0.56	119	0.00298
	15	1.15	277	0.00414
	20	2.23	355	0.00627
	25	3,43	431	0.00795
	30	5.48	490	0.01117
	35	7.81	542	0.01437
	40	10.51	590	0.01782
Wahiawa	15	0.04	314	0.00013
	20	0.10	398	0.00026
(Tropeptic Eutrusthox)	25	0.24	495	0.00048
	30	0.44	591	0.00074
	35	0.80	684	0.00117
	40	1.43	771	0.00185
	45	1.99	840	0.00356
	55	4.52	1010	0.00447
	60	5.72	1086	0.00527
	70	9.38	1212	0.00774
	75	11.30	1274	0.00887
	80	13.80	1324	0.01042
Kapaa	20	0.01	400	
	50	0.17	997	0.00017
(Typic Gibbsihumox)	75	0.37	1493	0.00025
	100	0.94	1981	0.00048
	110	1.41	2172	0.00065
	120	2.37	2353	0.00101
	140	3.84	2723	0.00141
	150	4.65	2907	0.00160
	175	8.58	3328	0.00258

Appendix Table 2. (Continued) Detailed phosphorus adsorption data for 8 Hawaiian soils[a]

Soil	Co (µg/ml)	C (µg/ml)	x/m (µg/g)	C/(x/m)
kaka	80	0.02	1600	0.000012
	120	0.21	2396	0.000088
Typic Hydrandept)	150	0.35	2993	0.000117
	200	0.59	3988	0.000148
	250	1.15	4977	0.000231
	300	1.95	5961	0.000327
	325	2.62	6448	0.000406
	350	3.21	6936	0.000463
	425	5.86	8383	0.000699
	450	7.64	8847	0.000864
	500	9.42	9812	0.000960
Naalehu	5	0.02	100	0.00020
	15	0.06	299	0.00020
(Typic Eutrandept)	25	0.32	494	0.00065
	30	0.38	592	0.00064
	35	0.56	689	0.00081
	40	0.83	783	0.00107
	50	1.61	968	0.00166
	60	2.82	1144	0.00247
	70	3.54	1329	0.00266
	80	4.45	1511	0.00294
	90	6.02	1680	0.00358
	100	7.80	1844	0.00423
	110	10.74	1985	0.00541
	120	12.66	2147	0.00590
Maile	100	0.11	1998	0.000056
	120	0.18	2397	0.000073
(Hydric Dystrandept)	200	0.69	3986	0.000173
	250	1.10	4978	0.000221
	280	1.46	5571	0.000262
	300	1.78	5965	0.000298
	325	2.00	6460	0.000309
	350	2.46	6951	0.000354
	400	3.74	7925	0.000472
	425	4.84	8403	0.000576
	450	5.45	8891	0.000613
	480	6.30	9474	0.000665
	500	6.84	9863	0.000694
	550	9.36	10813	0.000866
	600	12.84	11743	0.001093

Appendix Table 2. (Continued) Detailed phosphorus adsorption data for 8 Hawaiian soils[a]

Soil	Co (µg/ml)	C (µg/ml)	x/m (µg/g)	C/x/m
Hanipoe	40	0.09	798	-
	65	0.27	1295	-
(Typic Dystrandept)	80	0.48	1591	0.000300
	100	0.79	1984	0.000401
	120	1.21	2376	0.000511
	130	1.48	2571	0.000574
	140	1.78	2764	0.000644
	150	2.11	2958	0.000715
	160	2.53	3149	0.000805
	170	3.00	3340	0.000898
	175	3.27	3435	0.000952
	180	3.57	3529	0.001012
	200	4.74	3905	0.001214
	210	5.34	4093	0.001305
	225	6.27	4375	0.001433
	240	7.38	4652	0.001586
	250	8.64	4827	0.001790
	260	10.20	4996	0.00204
	280	12.48	5350	0.00233
	300	14.32	5714	0.00251
	325	17.47	6151	0.00284
	350	22.30	6554	0.00340

[a]Equilibration time - Lualualei - 8 days
Other soils - 6 days

Key: Co = Initial solution P concentration
C = Equilibrium solution P concentration
x/m = Amount of P adsorbed by the soil

Appendix Table 3. Detailed P adsorption data for 8 Indian soils[a]

Soil	Co (µg/ml)	C (µg/ml)	x/m (µg/g)	C/x/m
Black Soil, Coimbatore	1	0.12	18	0.0067
	2	0.24	35	0.0068
	3	0.56	49	0.0114
	5	1.02	80	0.0128
	7.5	1.80	114	0.0158
	10	2.79	144	0.0194
	15	5.34	193	0.0277
	20	8.99	220	0.0409
	25	11.60	268	0.0433
Black Soil, Kovilpatty	1	0.07	18	0.0041
	3	0.31	54	0.0057
	5	0.71	86	0.0082
	7.5	1.39	122	0.0113
	10	2.67	146	0.0183
	15	4.70	205	0.0229
	20	7.68	246	0.0312
	25	10.40	292	0.0356
	30	14.60	308	0.0474
	35	16.30	373	0.0437
Red Soil, Coimbatore	1	0.09	18	0.005
	2	0.20	36	0.006
	5	0.67	87	0.008
	10	2.15	157	0.014
	15	5.00	200	0.025
	20	8.89	222	0.040
	25	12.26	255	0.048
Red Soil, SVRP	1	0.10	18	0.006
	2	0.42	31	0.013
	3	0.96	41	0.024
	5	2.52	60	0.042
	10	6.60	88	0.075
	15	11.36	103	0.110
	20	16.60	108	0.154
	25	20.50	140	0.146
	30	26.00	140	0.186
	40	36.90	142	0.260
	50	46.00	180	0.255

Appendix Table 3. (Continued) Detailed P adsorption data for 8 Indian soils[a]

Soil	Co (µg/ml)	C (µg/ml)	x/m (µg/g)	$\frac{C}{x/m}$
Low Level Laterite, Pallathur	11.0	1.12	198	0.0057
	16.5	3.15	267	0.0118
	22.0	5.94	321	0.0185
	27.9	9.60	358	0.0268
	30.1	12.45	411	0.0303
	44.0	21.45	451	0.0476
	52.0	26.87	453	0.0593
	55.0	28.37	533	0.0533
	73.7	46.12	552	0.0836
	83.75	54.75	580	0.0944
	107.75	73.75	680	0.1084
Low Level Laterite, Vallam	2.2	0.01	44	0.0002
	5.5	0.13	107	0.0012
	11.0	1.40	192	0.0072
	15.5	3.30	264	0.0125
	22.0	6.41	312	0.0205
	27.5	10.32	344	0.0300
	33.0	13.00	400	0.0325
	44.0	22.75	425	0.0535
	49.5	27.25	445	0.0612
	55.0	30.37	493	0.0616
	77.0	51.25	515	0.0995
	88.0	56.25	635	0.0886
	110.0	76.25	675	0.1129
High Level Laterite, Doddabedda	25	0.03	499	0.00006
	30	0.07	599	0.00012
	35	0.16	697	0.00023
	37	0.20	746	0.00026
	40	0.24	795	0.00031
	50	0.54	989	0.00054
	55	0.88	1082	0.00082
	60	1.01	1180	0.00086
	70	1.61	1268	0.00117
	80	2.46	1551	0.00159
	90	3.49	1730	0.00202
	100	5.30	1894	0.00280
	112	7.39	2092	0.00353
	120	10.08	2198	0.00459
	150	21.98	2560	0.00859
	200	42.76	3145	0.01360

Appendix Table 3. (Continued) Detailed P adsorption data for 8 Indian soils[a]

Soil	Co (µg/ml)	C (µg/ml)	x/m (µg/g)	$\frac{C}{x/m}$
High Level Laterite, Nanjanad	5	0.03	99	0.00034
	10	0.11	198	0.00058
	15	0.23	295	0.00077
	25	0.78	484	0.00161
	30	1.16	577	0.00202
	35	1.78	664	0.00268
	40	2.56	749	0.00342
	45	3.60	828	0.00435
	50	5.25	895	0.00587
	55	6.33	973	0.00650
	65	10.14	1097	0.00924

[a]Equilibration time - Black Soils - 8 days
Other Soils - 6 days

Key: Co = Initial solution P concentration
C = Equilibrium solution P concentration
x/m = Amount of P adsorbed by the soil

Appendix Table 4. Effect of P adsorption on pH and the amount of sulfate and silica released by Wahiawa soil into the equilibrium solution[a]

P Adsorption Data				pH	Anions Released (mm/100g)	
Co (µg/ml)	C (µg/ml)	x/m (µg/g)	x/m (mm/100g)		SO_4	Si
10	0.21	196	0.63	5.65	0.039	0.063
15	0.95	278	0.90	5.87	0.054	0.084
20	1.70	366	1.18	5.95	0.094	0.128
25	2.83	444	1.39	6.02	0.100	0.151
35	7.48	547	1.71	6.06	-	0.152
40	12.51	550	1.72	6.06	-	0.158
45	14.78	601	1.94	6.06	-	0.191
50	18.85	623	2.01	6.08	0.135	0.213
55	19.20	713	2.30	6.13	-	0.236
60	23.56	729	2.35	6.17	-	0.251
65	26.60	765	2.47	6.17	-	0.257
75	33.30	831	2.68	6.11	0.146	0.268
85	41.30	871	2.81	6.11	-	0.289
90	44.20	916	2.95	6.06	0.186	0.309
95	47.87	940	3.03	6.06	-	0.323
100	52.37	953	3.07	6.03	0.175	0.325
120	72.00	960	3.10	5.92	0.121	0.333
150	97.75	1056	3.41	5.88	0.106	0.368

[a]12 hours equilibration in KH_2PO_4 medium.

Key: Co = Initial solution P concentration
C = Equilibrium solution P concentration
x/m = Amount of P adsorbed by the soil

Appendix Table 5. Effect of P adsorption on pH and the amount of sulfate and silica released by Akaka soil into the equilibrium solution[a]

P Adsorption Data				pH	Anions Released (mm/100g)	
Co	C	x/m				
(µg/ml)	(µg/ml)	(µg/g)	(mm/100g)		SO_4	Si
100	1.35	1973	6.36	4.90	1.26	0.10
150	5.03	2899	9.35	4.99	2.07	0.14
200	12.68	3746	12.08	5.15	2.29	0.16
225	16.58	4154	13.40	5.20	2.53	0.19
250	22.00	4560	14.71	5.25	2.69	0.20
275	30.91	4868	15.70	5.27	2.82	0.22
300	41.83	5163	16.65	5.32	3.01	0.22
325	51.75	5451	17.58	5.35	3.04	0.24
350	58.81	5681	18.32	5.35	3.09	0.25
375	69.80	6090	19.64	5.35	3.46	0.27
425	69.80	6604	21.30	5.36	3.72	0.30
450	97.99	7040	22.71	5.45	3.75	0.32
475	111.99	7246	23.37	5.45	3.81	0.36
500	137.65	7247	23.38	5.44	3.81	0.38
600	164.32	8714	28.11	5.44	4.09	0.41
750	275.30	9494	30.62	5.39	4.80	0.53
1000	401.00	11980	38.64	5.36	5.01	0.68

[a]12 hours equilibration in KH_2PO_4 medium

Key: Co = Initial solution P concentration
C = Equilibrium solution P concentration
x/m = Amount of P adsorbed by the soil

Appendix Table 6. Effect of P adsorption on pH and the amount of sulfate and silica released by Lualualei soil into the equilibrium solution[a]

P Adsorption Data				pH	Anions Released (mm/100g)	
Co (µg/ml)	C (µg/ml)	x/m (µg/g)	x/m (mm/100g)		SO_4	Si
1	0.67	7	0.02	7.74	0.026	0.001
5	2.58	48	0.15	7.68	-	0.030
10	6.11	78	0.25	7.67	0.049	0.043
15	9.44	114	0.37	7.67	-	0.071
20	13.00	140	0.45	7.67	-0.031	0.102
25	15.13	194	0.62	7.70	-	0.141
30	19.90	201	0.65	7.70	-	0.156
35	23.60	231	0.74	7.71	-	0.216
40	27.90	242	0.78	7.70	-0.192	0.240
45	31.20	290	0.93	7.70	-	0.293
55	38.00	337	1.09	7.60	-	0.375
60	43.00	340	1.10	7.50	-0.204	0.375
70	49.60	408	1.32	7.45	-0.255	0.496

[a]12 hours equilibration in KH_2PO_4 medium

Key: Co = Initial P concentration in solution
C = Equilibrium solution P concentration
x/m = Amount of P adsorbed by the soil

Appendix Table 7. Effect of temperature on P adsorption by Molokai and Red Soil, Coimbatore[a]

Equilibrium Temperatures								
10°C			25°C			35°C		
Co	C	x/m	Co	C	x/m	Co	C	x/m
				Molokai Soil				
2	0.12	38	2	.06	39	2	.06	39
5	0.31	94	5	.23	95	5	.14	97
10	0.92	182	10	.56	189	10	.40	192
15	2.16	257	15	1.15	277	15	.74	285
20	4.50	310	20	2.23	355	20	1.27	375
25	7.04	359	25	3.43	431	25	2.32	454
30	10.08	398	30	5.48	490	30	3.59	428
35	13.40	432	35	7.81	544	35	5.40	592
40	16.56	469	40	10.51	590	40	6.81	664
						45	8.59	728
				Red Soil, Coimbatore				
1	.10	18	1	.09	18	1	.09	18
2	.22	36	2	.20	36	2	.19	36
5	.89	82	5	.67	87	5	.51	90
10	3.10	138	10	2.15	157	10	1.69	166
15	6.80	164	15	5.00	200	15	3.68	226
20	11.47	171	20	8.89	222	20	6.86	263
25	14.19	216	25	12.26	255	25	10.76	285

[a]6 days equilibration in 0.01 M $CaCl_2$ + $Ca(H_2PO_4)_2$ medium

Key: Co = Initial solution P concentration (µg/ml)
C = Equilibrium solution P concentration (µg/ml)
x/m = Amount of P adsorbed by the soil (µg/g)

Appendix Table 8. Effect of temperature on P adsorption by Wahiawa soil[a]

Temperatures								
10°C			20°C			35°C		
Co	C	x/m	Co	C	x/m	Co	C	x/m
15.7	0.10	313	15.7	.04	314	15.7	.05	314
21.0	0.27	415	21.0	.18	416	21.0	.12	418
26.2	0.68	511	26.2	.41	517	26.2	.32	519
31.5	1.21	606	31.5	.78	615	31.5	.59	618
36.7	2.34	688	36.7	1.46	706	36.7	1.00	715
42.0	3.63	767	42.0	2.44	791	42.0	1.79	805
47.2	5.15	842	47.2	3.65	872	47.2	2.51	895
52.5	7.78	894	52.5	5.50	940	52.5	3.79	974
57.7	9.77	960	57.7	7.60	1003	57.7	5.22	1050
68.2	15.27	1059	63.0	9.33	1073	63.0	6.83	1123
73.5	18.52	1100	68.2	11.58	1133	68.2	8.65	1192
			73.5	14.09	1188	73.5	11.18	1296
			78.7	17.25	1229	78.7	12.92	1317
			84.0	19.88	1282	84.0	15.35	1373

[a]6 days equilibration in 0.01 M $CaCl_2$ + $Ca(H_2PO_4)_2$ medium

Key: Co = Initial solution P concentration (µg/ml)
C = Equilibrium solution P concentration (µg/ml)
x/m = Amount of P adsorbed by the soil (µg/g)

Appendix Table 9. Effect of temperature on P adsorption by a Hawaiian and two Indian soils[a]

Temperatures					
10°C			25°C		
Co (µg/ml)	C (µg/ml)	x/m (µg/g)	Co (µg/ml)	C (µg/ml)	x/m (µg/g)
		Kapaa Soil (Hawaii)			
50	0.15	997	50	.13	997
75	0.70	1399	75	.37	1493
90	1.66	1767	100	.90	1982
100	2.46	1951	110	1.25	2175
110	3.64	2127	120	1.81	2364
120	5.48	2290	140	3.36	2733
130	7.16	2457	150	4.56	2909
140	9.80	2604	160	5.67	3087
150	12.41	2752	175	8.10	3338
160	15.14	2897	200	13.26	3735
170	20.34	2993			
180	22.87	3143			
		Black Soil, Coimbatore (India)			
1	0.09	18	1	0.09	18
3	0.50	50	3	0.44	51
5	1.16	77	5	0.95	81
7.5	2.12	108	7.5	1.70	116
10	3.24	135	10	2.64	147
15	6.06	179	15	4.59	208
20	9.56	209	20	7.56	249
30	16.45	271	25	10.26	295
			30	12.90	348
		High Level Laterite, Doddabedda (India)			
30	0.17	596	30	0.04	599
37.5	0.39	742	37.5	0.19	746
50	1.20	976	50	0.51	990
55	1.77	1065	60	1.00	1180
60	2.31	1154	80	2.70	1546
70	3.71	1326	90	3.90	1722
80	5.85	1483	100	5.64	1887
90	8.91	1622	110	7.53	2049
100	11.82	1764	120	10.20	2194
110	15.74	1885	130	12.12	2358
120	20.94	1981			

[a]8 and 6 days equilibration for Black Soil and the other two respectively in 0.01 M $CaCl_2$ + $Ca(H_2PO_4)_2$ medium

Key: Co = Initial solution P concentration
C = Equilibrium solution P concentration
x/m = Amount of P adsorbed by the soil

Appendix Table 10. Effect of temperature on P adsorption by the Low Level Laterite soil[a]

Temperatures					
10°C			30°C		
Co	C	x/m	Co	C	x/m
5.5	0.65	97	2.2	0.02	44
11.0	2.00	180	5.5	0.18	106
16.5	4.70	236	11.0	1.04	199
22.0	8.65	267	16.5	2.81	274
27.5	12.47	301	22.0	5.82	324
30.2	15.17	308	33.0	13.69	386
33.0	17.19	316	38.5	17.08	428
38.5	20.97	351	44.0	21.06	459
44.0	24.90	382	49.5	24.45	501
55.0	35.02	400	55.0	29.67	507
60.5	40.37	403	60.5	34.33	523
71.5	49.51	440	71.5	43.82	554
			77.0	47.47	591

[a] 6 days equilibration in 0.01 M $CaCl_2$ + $Ca(H_2PO_4)_2$ medium

Key: Co = Initial solution P concentration (µg/ml)
C = Equilibrium solution P concentration (µg/ml)
x/m = Amount of P adsorbed by the soil (µg/g)

Appendix Table 11. Isosteric heat of phosphate adsorption of soils as a function of fractional surface coverage (θ)[a] calculated using P adsorption data of three temperatures

Soil	θ	$\Delta H_{x/m}$ KCal/Mole		
		Calculated between T's of		
		10, 25°C	10, 25 & 35°C	25, 35°C
Molokai	0.79	7.3	6.32	-
	0.89	8.8	8.99	8.81
	0.99	11.6	11.35	10.22
	1.09	13.2	12.66	10.73
	1.99	-	-	10.70
	1.29	-	-	11.25
Wahiawa	0.68	8.65	8.45	7.97
	0.74	8.70	8.88	7.10
	0.79	9.10	8.61	7.38
	0.84	8.78	8.46	7.87
	0.89	8.42	8.48	8.40
	0.95	10.63	9.90	8.54
Red Soil, Coimbatore	0.70	4.80	4.67	4.10
	0.82	6.30	6.21	5.75
	0.95	8.29	7.77	6.22
	1.20	10.90	11.60	12.10

$$a_\theta = \frac{\text{P Adsorbed + Surface P}}{\text{Langmuir's } b_{max}}$$

Appendix Table 12. The phosphate potential[a] of eight Hawaiian and eight Indian soils (30 minutes equilibration)

Soil	PO_4 potential
Hawaiian Soils	
Lualualei	8.07
Molokai	7.65
Wahiawa	8.03
Kapaa	8.40
Akaka	8.62
Naalehu	8.30
Maile	7.81
Hanipoe	8.13
Indian Soils	
Black Soil, Coimbatore	7.72
Black Soil, Kovilpatty	7.82
Red Soil, Coimbatore	8.30
Red Soil, SVRP	8.50
Low Level Laterite, Vallam	8.02
Low Level Laterite, Pallathur	8.00
High Level Laterite, Doddabedda	7.25
High Level Laterite, Nanjanad	7.54

[a]Phosphate potential = 1/2 pCa + pH_2PO_4

Appendix Table 13. Equilibrium solution concentration of calcium on shaking soils with 0.01 M $CaCl_2$ for phosphate potential estimations[a]

Soils	Calcium Concentration (Moles/Liter)
Hawaiian Soils	
Lualualei	0.0072
Molokai	0.0089
Wahiawa	0.0089
Kapaa	0.0094
Akaka	0.0092
Naalehu	0.0086
Maile	0.0082
Hanipoe	0.0100
Indian Soils	
Black Soil, Coimbatore	0.0095
Black Soil, Kovilpatty	0.0083
Red Soil, Coimbatore	0.0090
Red Soil, SVRP	0.0099
Low Level Laterite, Vallam	0.0093
Low Level Laterite, Pallathur	0.0097
High Level Laterite, Doddabedda	0.0094
High Level Laterite, Nanjanad	0.0098

[a]Equilibration time - 30 minutes

Appendix Table 14. Effect of phosphorus fertilizer on dry matter yields, and phosphorus concentration in Pearl Millet (Pennisetum typhoides) grown in pots on 8 Hawaiian soils

Soil	Adjusted P in Solution (µg/ml)	Fertilizer P applied (µg/g)	Yield (g/pot)	Phosphorus in plants %	Phosphorus in plants mg/pot
		Hawaiian Soils			
Lualualei	<0.022	0	0.04	0.09	<0.01
(Typic Chromustert)	0.022	10	0.04	0.08	0.03
	0.066	15	0.07	0.10	0.07
	0.200	40	0.18	0.14	0.25
	0.600	120	0.70	0.28	1.97
	1.800	270	1.50	0.47	7.16
Molokai	<0.022	0	0.53	0.38	2.01
(Tropeptic Torrox)	0.022	40	0.61	0.39	2.37
	0.066	58	0.60	0.41	2.46
	0.200	120	0.61	0.45	2.72
	0.600	255	0.70	0.57	4.01
	1.800	390	0.87	0.65	5.70
Wahiawa	<0.022	0	0.08	0.06	0.05
(Tropeptic Eutrusthox)	0.022	270	0.17	0.15	0.27
	0.066	350	0.22	0.23	0.51
	0.200	470	0.38	0.21	0.78
	0.600	645	0.94	0.50	4.61
	1.800	820	1.03	0.52	5.35

Appendix Table 14. (Continued) Effect of phosphorus fertilizer on dry matter yields, and phosphorus content of Pearl Millet (Pennisetum typhoides) grown in pots on 8 Hawaiian soils

Soil	Adjusted P in Solution (µg/ml)	Fertilizer P applied (µg/g)	Yield (g/pot)	Phosphorus in plants	
				%	mg/pot
Kapaa	<0.022	0	0.05	0.09	0.05
(Typic Gibbsihumox)	0.022	600	0.19	0.17	0.32
	0.066	810	0.35	0.22	0.76
	0.200	1070	0.49	0.25	1.23
	0.600	1670	0.75	0.67	5.06
	1.800	2300	0.92	0.61	5.61
Akaka	<0.022	0	.09	0.09	0.08
(Typic Hydrandept)	0.022	1640	.79	0.45	3.55
	0.066	2000	.82	0.48	3.94
	0.200	2360	.74	0.48	3.55
	0.600	4000	.78	0.63	4.91
	1.800	5800	.58	0.70	4.06
Naalehu	<0.022	0	0.07	0.10	0.07
(Typic Eutrandept)	0.022	250	0.18	0.28	0.49
	0.066	300	0.19	0.27	0.52
	0.200	420	0.30	0.34	1.04
	0.600	645	0.74	0.65	4.78
	1.800	1010	0.86	0.71	6.15
Maile	<0.022	0	0.07	0.08	0.06
(Hydric Dystrandept)	0.022	1120	0.79	0.53	4.23
	0.066	1690	0.81	0.63	4.60
	0.200	2460	0.82	0.82	6.64
	0.600	3660	0.87	0.82	7.09
	1.800	6120	0.92	0.92	8.48

Appendix Table 14. (Continued) Effect of phosphorus fertilizer on dry matter yields, and phosphorus content of Pearl Millet (Pennisetum typhoides) grown in pots on 8 Hawaiian soils

Soil	Adjusted P in Solution (µg/ml)	Fertilizer P applied (µg/g)	Yield (g/pot)	Phosphorus in plants	
				%	mg/pot
Hanipoe	<0.022	0	0.13	0.02	0.03
(Typic Dystrandept)	0.022	530	0.37	0.30	1.13
	0.066	700	0.69	0.48	3.33
	0.200	1080	0.73	0.58	4.26
	0.600	1730	0.72	0.76	5.50
	1.800	2720	0.76	0.86	6.54

Appendix Table 15. Effect of phosphorus fertilizer on dry matter yields, and P content of Pearl millet grown in pots on 4 Indian soils

Soil	Adjusted P in Solution (µg/ml)	Fertilizer P applied (µg/g)	Yield (g/pot)	P in the Plant	
				%	mg/pot
		Indian Soils			
Black Soil, Coimbatore	<0.022	0	0.06	0.09	0.05
	0.022	5	0.12	0.10	0.13
	0.066	12	0.17	0.20	0.33
	0.200	25	0.43	0.33	1.43
	0.600	50	0.89	0.38	3.29
	1.800	113	1.13	0.52	5.91
Red Soil, Coimbatore	<0.022	0	0.07	0.12	0.08
	0.022	48	0.34	0.21	0.71
	0.066	55	0.48	0.29	1.40
	0.200	76	0.81	0.31	2.51
	0.600	120	1.69	0.53	8.91
	1.800	180	1.86	0.45	8.47
Low Level Laterite, Vallam	<0.022	0	-	-	-
	0.022	65	0.12	0.13	0.16
	0.066	90	0.20	0.22	0.59
	0.200	122	0.41	0.21	0.69
	0.600	160	0.85	0.24	1.79
	1.800	210	1.11	0.28	3.14
High Level Laterite, Doddabedda	<0.022	0	-	-	-
	0.022	430	0.22	0.24	0.52
	0.066	580	0.59	0.28	1.69
	0.200	740	0.76	0.31	2.33
	0.600	1015	1.23	0.78	9.66
	1.800	1420	1.14	0.81	9.25

Appendix Table 16. Effect of phosphorus fertilizer on dry matter yields, and phosphorus content of Desmodium intortum, grown in pots on three Hawaiian soils

Soil	Adjusted P in solution (µg/ml)	Fertilizer P applied (µg/g)	Yield (g/pot)	Phosphorus	
				%	mg/pot
Lualualei	0.022	10	0.144	0.11	0.17
(Typic Chromustert)	0.066	15	0.168	0.14	0.24
	0.200	40	0.190	0.12	0.23
	0.600	120	0.302	0.25	0.75
	1.800	270	0.605	0.38	2.32
Wahiawa	0.022	270	0.170	0.22	0.37
(Tropeptic Eutrusthox)	0.066	250	0.171	0.14	0.24
	0.200	470	0.417	0.34	1.41
	0.600	645	0.460	0.37	1.72
	1.800	820	0.616	0.43	2.64
Akaka	0.022	1640	0.277	0.24	0.40
(Typic Hydrandept)	0.066	2000	0.305	0.22	0.38
	0.200	2360	0.554	0.27	1.22
	0.600	4000	0.574	0.28	1.38
	1.800	5800	0.484	0.32	2.00

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